Kinetic Study of Ethylene Oxidation Using Silver Catalyst in a Berty Reactor

by

Muhammad Saud Al-Ahmadi

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
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MASTER OF SCIENCE

In

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Al-Ahmadi, Muhammad Saud, M.S.

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300 N. Zeeb Rd.
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This thesis, written by MUHAMMAD SAUD AL-AHMADI under the direction of his Thesis Committee, and approved by all its members, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN CHEMICAL ENGINEERING.

Abdullah Al-Zahrani
Dean
College of Graduate Studies

Date: Dec. 17, 1985

Department Chairman

Thesis Committee

M.A. Saleh
Chairman (Dr. Muhammad Al-Saleh)

Member (Dr. Selahattin Gultekin)

Member (Dr. Erdogan Alper)

to my respected

mother and father

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ABSTRACT

The reaction of ethylene oxidation was studied on a silver catalyst supported on alumina in a Berty reactor (CSTCR).Rate expresions were fitted to the data free of any physical resistances .Reaction products were ethylene oxide , carbone dioxide , and water . The rate expressions are as follows :

1) Rate of conversion of ethylene to ethylene oxide :

$$r_1 = \frac{(1.354\times10^{3})\exp(-9010/T)(P_{O2})^{0.5}(P_{C2H4})^{0.6}}{1+(2.88\times10^{-2})\exp(2400/T)(P_{CO2})}$$

2) Rate of conversion of ethelene to carbon dioxide :

$$r_2 = \frac{(6.30\times10^{3})\exp(-10800/T)(P_{O2})^{0.5}(P_{C2H4})^{0.5}}{1+(1.57\times10^{-2})\exp(1530/T)(P_{CO2})}$$

The reaction rates were measured using a feed containing ethylene (3-6.5 %) , oxygene (18-19.5%) and the balance being nitrogen . The operating temperatures were varied from 513 K to 593 K and the operating pressure was kept at 300 PSIG . Flow rates were varied from 9.25 to 275 l/hr at STP . THe catalyst used was in the form of cylindrical pellets (1/8 x 1/8 in.) containing 8% siver supported on α alumina ; and supplied by Harshaw/Filtrol Partnership .

Behavior of selectivity of ethylene oxide vs total conversion of

ethylene was observed at different temperatures and it was found that selectivity decreases with the increase in conversion of ethylene . Temperature was found to have a negligible effect on the selectivity at the same conversions .

chapter 1

INTRODUCTION

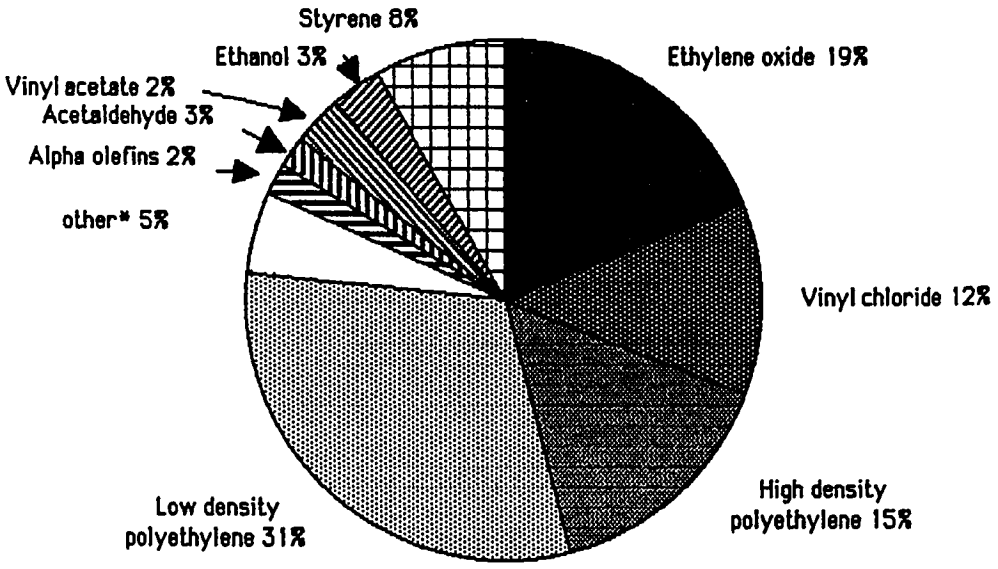
1.1 *Importance of ethylene oxidation*

Ethylene oxide is one of the major individual compounds produced from ethylene (Figure1.) . It is an important organic intermediate and probably the most verstile petrochemical at the disposal of industry today . Table-1 and Table-2 show the important ethylene oxide derivatives .

The production of ethylene glycol from ethylene oxide is predicted to utilise 50% of ethylene oxide production. Nonionic surfactants , the fastest growing market for ethylene oxide , are predicted to utilise about 11% of ethylene oxide production .

1.2 *Ethylene Oxidation Processes*

The old industrial chlorohydrin process for the synthesis of ethylene oxide consisted of the reaction between ethylene and chlorine in the presence of steam , followed by the hydrolysis of ethylene chlorohydrin with soda lime . Today , all commercial ethylene oxide (EO) is produced by vapor phase direct oxidation of ethylene using a silver catalyst . As an oxygen sourse in the direct oxidation process , either air (air oxidation process) , or pure oxygen (oxygen oxidation



*Ethylene dibromide,ethylene chloride.

Figure 1. Estimated utilization of ethylene demand in 1980 .

Table -1 Important ethylene oxide derivatives

compound	percentage consumption
Surfactants	11%
Higher glycols	8%
Ethylene glycol	58%
Glycol ethers	7%
Ethanolamines	6%
Others	10%

Table-2 Important ethylene glycol derivatives

compound	percentage consumption
Antifreeze	49%
Polyester fibre	41%
Polyester film	3%
Industrial fluids	6%
Polyester resins	1%

process) is being used .

Union Carbide Corp. developed the first air oxidation process in 1937 . In 1958 , shell developed the first oxygen oxidation process . Figure (2) and Figure(3) show both type of processes .

Main differences [38] between the two processes are only in the oxidation section in which an air compressor and a purge reactor system are needed for the air oxidation and a carbone dioxide removal system is needed for the oxygen oxidation .

The operation of the reactor [38] is fundamentally the same for both process . Fresh ethylene , recycle gas and air (in case of the oxygen oxidation) are mixed and fed to the main reactor . The reactor is a shell-and-tube type , comprising several thousands tubes made of mild stainless steel with the length of about 10 m and the inside diameter of 20 to 40 mm . A silver catalyst is placed in the tubes to a height of several meters .

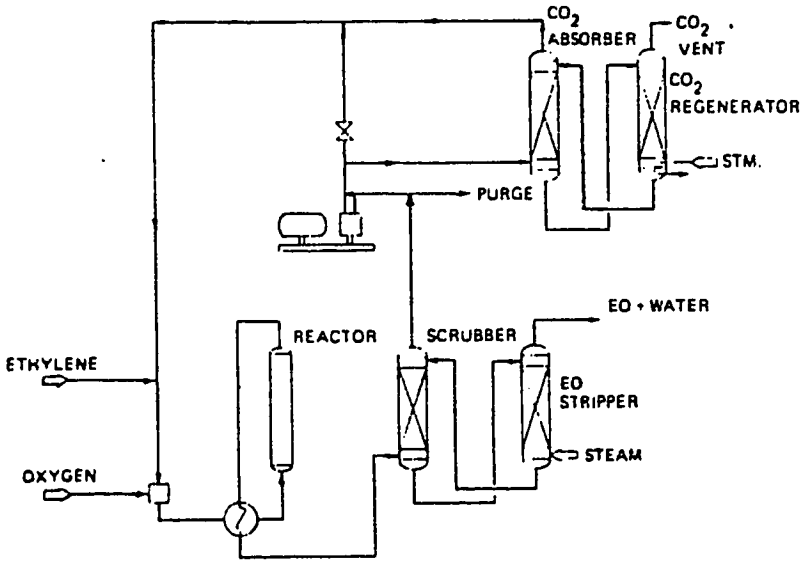


Figure 2. Ethylene oxide process (oxygen case).

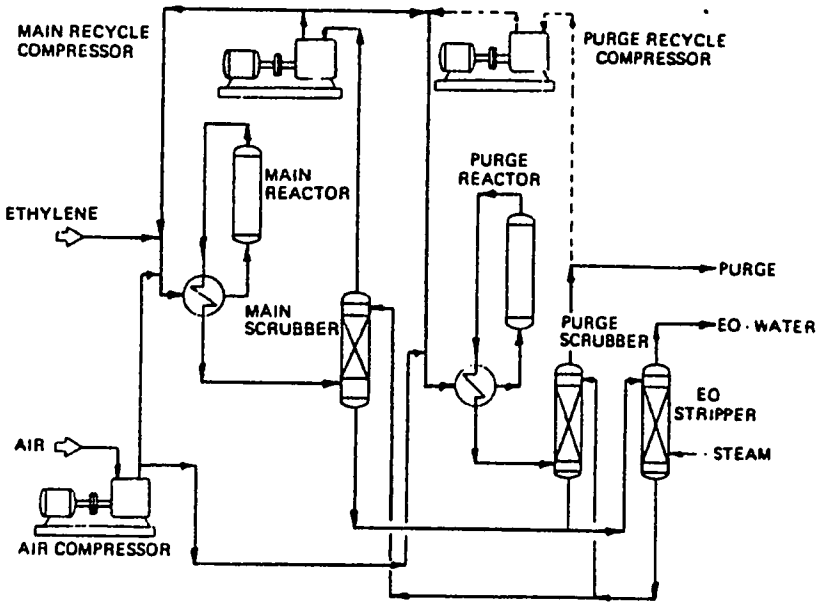


Figure 3. Ethylene oxide process (air case).

1.3 *Thesis objectives*

1) Literature survey .

2) Adjusting , and operating the high pressure reactor system , including the Berty reactor ; which is run for the first time . The reactor system is composed of so many sections .

3) Operating and calibrating the Perkin Elmer gas chromatograph with data console which is operated for the first time ; searching for a column which can separate the reactant and product gases [O_2 , N_2 , CO_2 , C_2H_4 , C_2H_4O] ,and then calibration .

4) Obtaining kinetic data for ethylene oxidation , free of any physical resistance using a Berty reactor [CSTCR] .

5) The development of kinetic models and the determination of the constants and activation energies for both reactions (partial and complete oxidation).

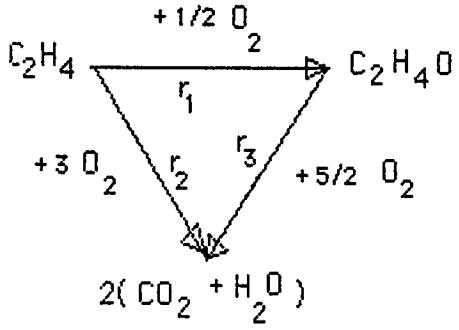
6) The selectivity to ethylene oxide is studied as a function of conversion and reaction conditions such as temperature .

chapter 2

LITERATURE SURVEY

2.1 *Ethylene oxidation chemistry and thermodynamics*

Ethylene oxide (EO) is produced by air or oxygen oxidation of ethylene over silver catalyst . The only by-products are carbon dioxide and water . The net work of the reactions can be described by the following :



The rate of the oxidation of ethylene oxide (r_3) is very small compared to the partial and total oxidation of ethylene .The chemical equations of the last two reactions are as the following :

At 550K in KJ/mol

The partial ethylene oxidation :

$C_2H_4 + 1/2\ O_2$ -------- C_2H_4O $\Delta H = -117$

$\Delta G = -50.6$

The total ethylene oxidation :

$C_2H_4 + 3\ O_2$ --------- $2\ CO_2 + 2\ H_2O$ $\Delta H = -1217$

$\Delta G = -1249$

According to the above , the chemical equilibrium for the reactions heavily favors the products . Also , it can be seen that the heat generated by the total oxidation reactions is much higher than the heat produced by the epoxidation .

2.2 *Adsorption characteristics of reactants and products on the catalyst surface*

Of all the reactants and products , the adsorption of oxygen is probably the most important one . Considerable amount of litrature is focused on the adsorption of oxygen on silver catalyst and it is greatly controversial . In addition to what can be obtained about the role of oxygen on the catalyst surface ,the adsorptive characteristics of oxygen on silver also can provide a means of obtaining the free metalic

surface of silver on supported silver catalysts through selective chemisorption .

What has concerned most investigators of interactions between silver and oxygen is the adsorption-desorption phenomena on silver powders and films(39,40-42), determination of the heats of adsorption (39,40-47) , work function changes upon adsorption (46,48-53), and the reactivity of different crystalline faces of silver(54-56).

Different experimental methods and techniques of surface science have been used to study the adsorption of oxygen on silver surfaces . These methods include Auger electron spectroscopy(50,56) , low energy electron diffraction (50,56,57) , microgravimetry (39,41), isotopic exchange (58),production of thin films (59),thermal desorption (39,41),electron spin resonance (60), infrared spectroscopy (43). The methods which have been most extensively used to clean the silver surfaces for oxygen adsorption include outgasing in ultrahigh vacuum, evaporation ,hydrogen reduction , and ion bombardment.

Many investigators attempted to determine what kind of oxygen species are adsorbed on silver surfaces where this is of special importance for catalytic oxidation of ethylene ;it has been a matter of considerable debates . It is generally accepted today that the chemisorption of oxygen on silver is in part dissociative and in part nondissociative. Accordingly, the most probably adsorbed states (61)include the species O_{2-} , O_2^{2-}, O^- , and O^{2-} .

Different techniques were employed to measure the rate of oxygen adsorption and desorption : volumetrically by Smeltzer et al. (62),gravimetrically by Czanderna(63,39,41), and manometrically by Kilty et al. (43). One or more breaks were reported in their kinetic curves ,which suggest several adsorbed states of oxygen on silver . Arrhenius plots of the oxygen adsorption on silver are shown in Figures (4)and (5) . Figure 4 is a reproduction of Czanderna's (62) data for an oxygen surface coverage of 0.77 . Figure 5. was constructed from plots of the rate of oxygen adsorption as a function of the amount of oxygen adsorbed reported by Kilty et al. (43) for surface coverage of 0.4 .Although one break is shown in each of these figures , a second break is claimed by the authors to occure at initial , very rapid oxygen adsorption . Both authors (62,43) agree that activation energies depend very slightly on the degree of surface coverage . Also,Figure 6. shows the heat of adsorption on pure silver at variuos concentrations of oxygen (44) .

The adsortption characteristics of the other species involved in the oxidation of ethylene ,other than oxygen , have not been studied extensively . Although many investigators (64,65,66-69) agree that ethylene is not adsorbed on reduced metallic silver , nevertheless , there is a strong evidence (66,68-71) that ethylene adsorbs on an oxygen covered silver surface , where oxygen adsorption has previously taken place , as well as on a silver surface contaminated with chlorine (72).

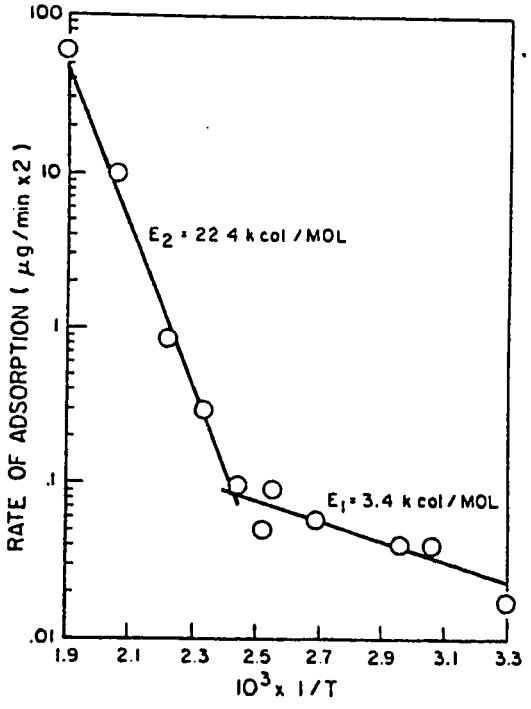


Figure 4. Arrhenius plot for a surface coverage of 0.77 oxygen

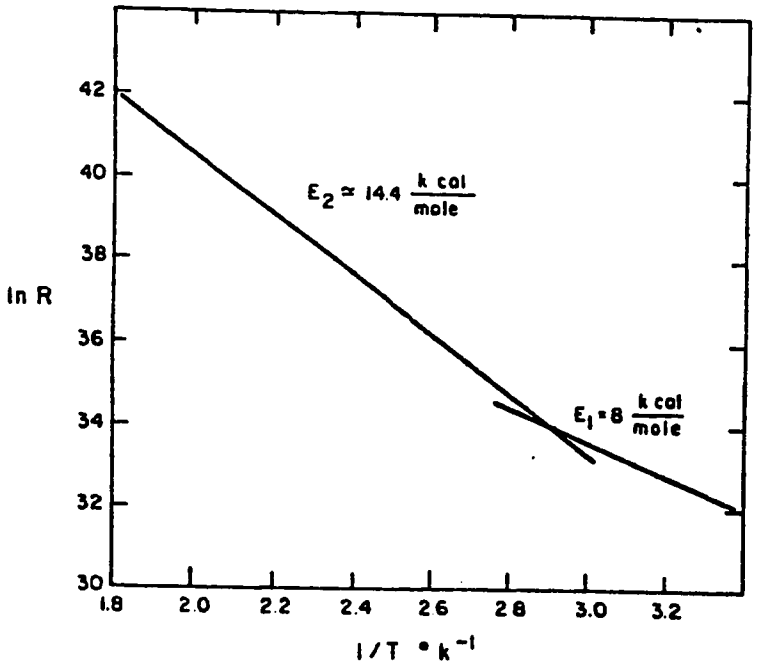


Figure 5. Arrhenius plot for a surface coverage of 0.4. Constructed from Kilty et al.'s [9] (R = Rate of oxygen adsorption)

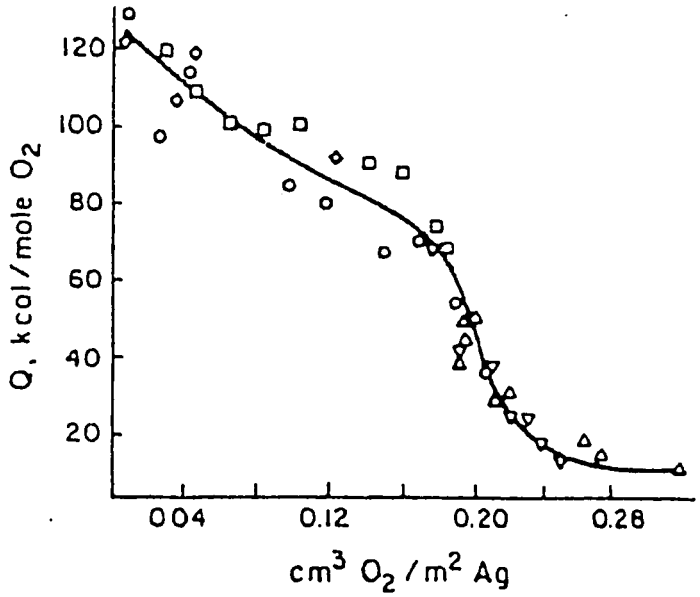


Figure 6. Heat of adsorption of oxygen on pure silver. After Ostrovskii and Temkin [44].

Force and Bell (66) , using infrared spectroscopy techniques , observed that ethylene adsorbs on an oxygenated silver surface without rupture of the C=C bond . No adsorption was observed on a completely reduced silver surface . Silver ions were considered to be the adsorption sites(28)

It is well established that each of the three reaction products adsorbs on silver oxide or on oxygenated silver surfaces (64,70,73). There is also a good evidence (64,3,68) that ethylene oxide adsorbes readily on clean metallic silver . Force and Bell (66) reported evidence in the form of infrared spectra that CO2 adsorbs in three configurations , one with the molecule parallel to the surface and two others in which CO2 interacts with adsorbed oxygen atoms to form mono-and bidentate carbonates (28)

2.3 *Ethylene oxidation kinetics*

Extensive literature is available on ethylene oxidation kinetics over silver catalyst . Different systems have been used ; static , flow , differentional , and recycle with various catalysts , feed ratios , and additives .

Twigg [3] ; in 1945 ; was the first to study the kinetics of ethylene oxidation in detail using air and glass wool fibers coated with silver at temperatures ranging from 473 to 573 K . Both static and flow systems were used . The following kinetic expressions were obtained :

$$r_{EO}=k_1(P_{C2H4})^{0.45}(P_{O2})^{0.55} \qquad (1)$$

$$r_{CO2}=k_2(P_{C2H4})^{0.3}(P_{O2})^{1.1} \qquad (2)$$

where

r_{EO} = ethylene reaction rate .

r_{CO2} = carbon dioxide reaction rate .

P_i = partial pressure of compound i .

k_1; k_2 = reaction rate constants .

Wan Shen-Wa [7] in 1958 used a reactor constructed from a stainless steel tube . Temperature ranged from 513 to 533 K and the catalyst was Silver promoted with Barium on alumina . Kinetic expression obtained was

$$r_{EO}=k_1(P_{C2H4})^{0.3}(P_{O2})^{0.7} \qquad (3)$$

where

r_{EO}= reaction rate of ethylene oxide .

p_i = partial pressure of compound i .

k = reaction rate constant .

Also , in 1958 Kurilenko [11] studied the kinetics of ethylene oxidation using a recirculating -flow reactor . Temperature was 491 K and the total pressure was 14.7 psia . Using a mechanism taken in part from their own work , and in part from others , the following kinetic expression was obtained :

$$r_{EO}=\frac{k1(P_{C2H4})}{1+r(P_{C2H4})[1+K3(P_{C2H40})]/(P_{O2})+K1(P_{C2H4})/K3+K5(P_{C2H40})+K6(P_{H20})+K7(P_{C02})} \qquad (4)$$

where

r_{EO}= reaction rate of ethylene oxide .

P_i = partial pressure of compound i .

k = reaction rate constant .

K_i = adsorption equilibrium constant of compound i .

Here r is (k1+6K2)/2K4 . The rate to CO2 is the same as the above , except that k1 in the numerator is replaced by K2

Fognani [10] ,in 1959 , using a catalyst consisted of Silver promoted with Barium on alumina at temperatures of 513 and 533 K ; obtained the following kinetic expressions :

$$r_{EO}=k_1(P_{O2}) \qquad (5)$$

$$r_{CO2}=k_2(P_{O2})/[1 + K(P_{O2})] \qquad (6)$$

where

r_{EO} = reaction rate of ethylene oxide .

r_{CO2}= reaction rate of carbon dioxide .

P_i = partial pressure of compound i .

k_1 ; k_2 = reaction rate constants .

K_i= adsorption equilibrium constant of compound i .

In 1970 , Alfani [30] studied the kinetics of ethylene oxidation by air over a commercial unmoderated silver catalyst at temperature ranging from 433 to 573 K . The reaction tookplace in a carberry reactor . The data were correlated and the following equations were presented for the conversion to ethylene oxide and carbon dioxide :

$$r_{EO}=k_1(P_{C2H4})^{0.5} \quad (7)$$

$$r_{CO2}=k_2(P_{C2H4})^{0.25} \quad (8)$$

where

r_{EO} = reaction rate of ethylene oxide .

r_{CO2} = reaction rate of carbon dioxide .

P_i = partial pressure of compound i .

$k_1 : k_2$ = reaction rate constants .

Also , Kenson [35] , in 1970 , investigated the reactions of ethylene oxidation over silver catalyst supported on alumina pellets at temperature from 448 to 523 K and at ethylene concentrations much higher than oxygen . Static and flow systems were employed . The reactions tookplace in a carbon steel tube .

Kinetic equations obtained were

$$r_{EO}=k_1(P_{O2}) \quad (9)$$

$$r_{CO2}=k_2(P_{O2}) \quad (10)$$

$$r_{EO-CO2}=k_3(P_{C2H4O}) \quad (11)$$

where

r_{EO} = reaction rate of ethylene oxide .

r_{CO2} = reaction rate of carbon dioxide .

r_{EO-CO2} = reaction rate of ethylene oxide to carbon dioxide .

P_i = partial pressure of compound i .

k_1 ; k_2; k_3 = reaction rate constants .

In 1971 , klugherz [29] used a differential reactor fabricated from stainless steel tubing . Temperature control was provided by immersing the reactor in an electrically heated fluidized bed of sand . The catalyst used was silver supported on alumina . Operating temperature was 493 K . The following were presented :

$$r_{EO}=k_1(P_{C2H4})(P_{O2})^{1.5} \quad (12)$$

$$r_{CO2}=k_2(P_{C2H4})(P_{O2})^{2} \quad (13)$$

where

r_{EO} = reaction rate of ethylene oxide .

r_{CO2} = reaction rate of carbon dioxide .

P_i = partial pressure of compound i .

k_1 ; k_2 = reaction rate constants .

Metcalf [36] , in 1972 , studied the ethylene oxidation using a differential reactor using silver supported on alumina as a catalyst . Operating temperature was 492 K . Also , the behaivior of varios inhibitors including ethylene , carbon dioxide , water and dichloroethylene was investigated . The following equations were presented :

at low O2 concentrations :

$$r_{EO} \sim k_1 (P_{C2H4})(O2)^{1.5} \qquad (14)$$

at high O2 concentrations :

$$r_{EO} \sim k_2 (P_{C2H4})(P_{O2})^{-0.3} \qquad (15)$$

where

r_{EO} = reaction rate of ethylene oxide .

P_i = partial pressure of compound i .

k_1 ; k_2 = reaction rate constants .

In 1973 , Verma [90] used a reactor which was made of a stainless steel tube , surrounded by a jacket through which a heating oil maintained at high temperature was kept circulating . Both pulse and steady state runs were employed . Catalyst used was in the form of a precipitated powder and the operating temperature was 494 K . Rate equations obtained were :

$$r_{EO}=k_1(P_{C2H4})^{-0.03}(P_{O2})^{0.91} \qquad (16)$$

$$r_{CO2}=k_2(P_{C2H4})^{-0.2}(P_{O2})^{1.1} \qquad (17)$$

where

r_{EO} = reaction rate of ethylene oxide .

r_{CO2} = reaction rate of carbon dioxide .

P_i = partial pressure of compound i .

k_1 ; k_2 = reaction rate constant .

Dettiler , in 1979 , investigated the kinetics of ethylene oxidation by air over a supported silver catalyst in the temperature range 490 to 620 K under constant oxygen partial pressure . The reaction tookplace at a pyrex U-tube reactor.

rate eqution obtained were :

$$r_{EO}=k_1(P_{C2H4})/[(1+K(P_{C2H4})] \quad (18)$$

$$r_{CO2}=k_2(P_{C2H4})/[1+K(P_{C2H4})] \quad (19)$$

$$r_{EO-CO2} = k_3(P_{C2H40}) \quad (20)$$

where

r_{EO} = reaction rate of ethylene oxide .

r_{CO2} = reaction rate of carbon dioxide .

r_{EO-CO2} = reaction rate of ethylene oxide to carbon dioxide .

P_i = partial pressure of compound i .

k_1 ; k_2; k_3 = reaction rate constants .

K_i = adsorption equilibrium constant of compound i .

Table-3 shows E_{EO} and E_{CO2} of different investigatores .This table indicates that activiation energies reported are varying considerably .

Table-3 Activation energies for the partial and complete Oxidation reaction of ethylene over Silver Catalysts

Catalyst	Activation energy(kJ/mole)	
	C2H4O	CO2+H2O
Ag,not described	63	89
Ag,Ba promoted	50	63
Ag,on alumina , Ba	79	
Ag promoted	79	90
Ag,evaporated film	109	123
Ag, on alumina	90	121
Ag,on glass wool	96	
Ag,on corundum	90	142
Silver oxide	63	56
Ag,throughly cleaned		88

2.4 *Ethylene oxidation mechanism*

Great difficulites have encounterd investigators who attempted to explain the kinetics and mechanism of the partial and complete oxidation reactions of ethylene over silver catalysts . These include : (1) the complexity of the reactions and thier sensitivity to the feed composition ; (2) the explosive nature of the ethylene -oxygen mixture ; (3) the sensitivity of the catalyst to traces of chlorine , sulfur , and other elements often presents as impurities in the feed gases or on the catalyst ; (4) large heats of reaction which causes deviations from isothermal conditions ; and (5) difficulties in characterizing the catalyst.

The main debates about the mechanism of the selective oxidation of ethylene catalyzed by silver primarily centers around the type and the exact role of the oxygen species chemisorbed on the catalyst surface [74,43,64]. Significant debate [3,70,64] was also focused on the chemisorption of ethylene on silver under reaction conditions and the state of the ethylene molecule which participates in the reaction (28). Many mechanisms , some involving a single site and others involving dual sites , have been proposed ; they also involve chemisorbed atomic or molecular oxygen or both , but none of the mechanisms has found general acceptance . Nevertheless , most investigators appear to agree that the rate -controlling step is a surface reaction , independent of adsorption or desorption rates .

It was concluded by Twigg(3) ,who was the first to study the

kinetics of this system in detail , that the reaction takes place via the interaction of gaseous or weakly adsorbed ethylene with one adsorbed oxygen atom to form ethylene oxide or with two adsorbed oxygen atomes to form intermediates which are rapidly oxidized to carbon dioxide and water and the slowest step in the entire series was the rate of oxygen adsorption . Figures (7) and (8) shows such schemes . The latter conclusion is not corroborated , however , by any of the more recent studies (28). To support his conclusion that the ethylene participates from the gas phase or from a weak van der Waals type adsorbed state ,Twigg found no measurable adsorption of ethylene on the catalyst , no recoverable carbonaceous deposite upon heating the catalyst in oxygen , and no hydrogenation of ethylene on the catalyst even though it adsobed hydrogen .

A similar mechanism where both reactions proceed via interactions of gaseous ethylene molecules with single adsorbed oxygen atomes was proposed by Orzechowski and MacCormac (8) . They postulated two parallel reaction pathways of different activation energy requirments but with a common initiation step to form adsorbed ethylene oxide . Ethylene oxide then would either desorb or isomerize to acetaldehyde which would be oxidized rapidly to carbon dioxide and water(28) . They also found , however , that some of the carbon dioxide produced arises from further oxidation of ethylene oxide [ ] ,in agrement with the work of Twigg[3] and of Margolis and Rogiskii [75] .

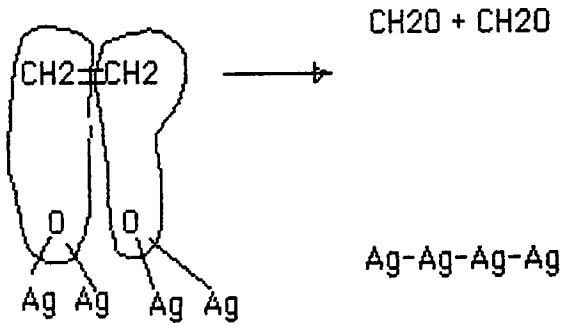


Figure 7. Scheme suggested by Twigg [3] for the production of carbon dioxide

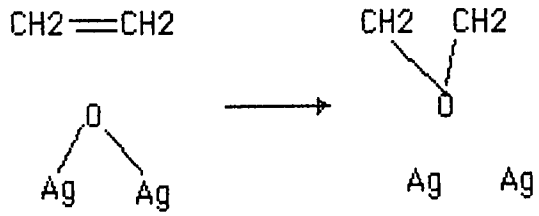


Figure 8. scheme suggested by Twigg [3] for the production of ethylene oxide

Many investigators supported the observation that both atomic oxygen (O-). , and moleccular oxygen ,(02-) , are adsorbed on the surface of silver catalyst. Therefore , mechanisms were proposed where one or both of the reactions proceed via these species . Based on their kinetic investigation , Klugherz and Harriott proposed a Langmuir -Hinshelwood type mechanism according to which the reactions take place between adsorbed ethylene and an oxygen molecule adsorbed on active sites formed by the dissociative adsorption of a lower layer of oxygen on metallic silver . Metcalf and Harriott [36] proposed that the mechanisms of both reactions are closely related , and thus they applied the same kinetic model to both . According to their view , the rate-determing step is a bimolecular surface reaction between adsorbed ethylene and adsorbed molecular or atomic oxygen . Similar types of mechanisms have also been reported in Refs(70,71,).Spath[76], based on the same type of dual site mechanism,suggested that ethylene oxide is produced via molecular oxygen chemisorbed on adjacent sites on a fully oxidized silver surface whereas carbon dioxide is produced via a chemisorbed oxygen atom.(28).

The role of an adsorbed oxygen molecule in the partial oxidation reaction and an adsorbed oxygen atom in the complete oxidation reaction is also reported by the molecular orbital calculations of Beran et al.[77] and by the data of Herzog[78] . The latter author compared the reactions of ethylene with oxygen and with nitrous oxide over silver catalyst . Although significant yields of ethylene oxide

were obtained by reactions with oxygen , none was obtained with nitrous oxide . Herzog concluded that nitrous oxide decomposes to form only atomic oxygen and argued that chemisorbed molecular oxygen is therefore responsible for the partial oxidation reaction , whereas atomic oxygen is responsble for the complete oxidation reaction . Identical results were also obtained by Imre[79] . It had been shown much earlier , however , that the decomposition of nitrous oxide on oxide surfaces produces both atomic and molecular oxygen , a result which tends to refuse the reasoning of Herzog and Imre.

Ionov et al .[80] reported that pressure had no effect on the kinetics of the reactions In their investigation of the oxidation of ethylene over a silver catalyst at moderate pressure (14.7to 235 psia) . They cite the pulse-method experiments of Mikami et al. [81] as confirmation of their assumption of direct gas- phase participation by ethylene , and a Rideal-Eley mechanism is proposed according to which ethylene enters the reaction directly from the gas phase and reacts reversibly with molecular oxygen adsorbed on two silver surface atoms to produce adsorbed ethylene oxide . Carbon dioxide and water are produced through an adsorbed vinyl alcohol intermediate which is formed . The existence of a vinyl alcohol intermediate is also supported by Kurilenko et al. [11] from their kinetic study using a circulating -flow method .

Kilty et al. [43] and Ayame et al. [82] proposed a Rideal-Eley rather than a Langmuir-Hinshelwood mechanism for the formation of

ethylene oxide (see Figure 9) .According to their conclusions , the adsorbed oxygen molecule ,(O2-)ads. , is suitably polarised to satisfy the nucleophilic properties of the incoming ethylene molecule and thus to produce ethylene oxide and an adsorbed oxygen atom , (O-)ads. .Carbon dioxide and water are produced from the reaction of ethylene and adsorbed oxygen atoms. They further argue from their own studies of the complex formed between the olefin and silver salts that ethylene strongly adsorbed onto surface oxygen species .

A wide variety of pulsed experiments which perturbed a steady-state operation were conducted by Kobayashi et al. [31] . They showed that a considerable amount of ethylene is revesibly adsorbed but that this adsorbed ethylene does not react with oxygen . They concluded that it is the gaseous ethylene that does react . The main criticism of their work is that their experiments were conducted at temperatures (353 to 433 K) lower than the usual range of interest(453 to 573 K). However,they argued that the top range of their experiments was sufficiently close to the usual temperature interval that their results could reasonably be expected to hold at the higher temperatures . From these experiments they concluded a Rideal-Eley type of mechanism with the surface reaction controlling . In their view , ethylene oxide is produced by reaction of gaseous ethylene and adsorbed diatomic oxygen , whereas carbon carbon dioxide and water are formed via adsorbed intermediate ; they speculated that the latter could be acetic acid, which is produced by the reaction of gaseous ethylene and adsorbed atomic oxygen . The

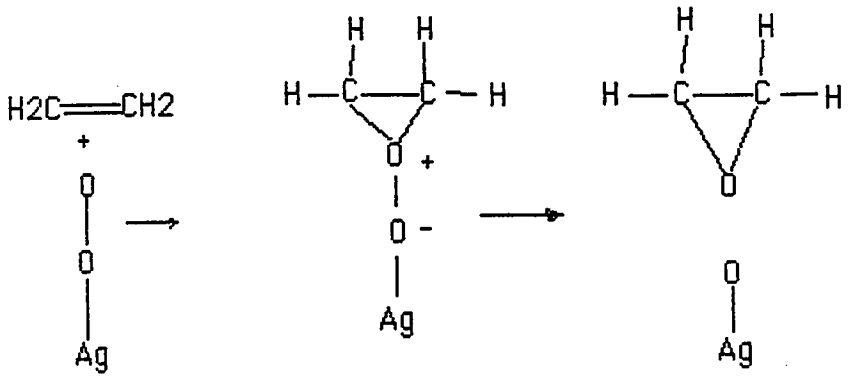


Fig. 9- Scheme suggested by Kilty [43] for the production of ethylene oxide

further oxidation of the intermediate proceeds via adsorbed molecular oxygen . The existence of an acid intermediate during the complete oxidation of the ethylene was detected in a later study by Kobayashi et al. [83] . The acetic acid intermediate was desorbed from the catalyst surface in a stream of pure hydrogen , but it decomposed to carbon dioxide and water in a mixture of hydrogen and oxygen .

Although Micami et al. (81) considered a mechanism based on gaseuos ethylene , it should be noted that their pulse experiments only excluded the participation of strongly adsorbed ethylene . Their results , however , do not exclude the participation of other adsorbed Species (for example : weakly adsorbed ethylene) . The participation of adsorbed species is revealed by more recent spectroscopic investigations [66] and experiments with deuterium-labeled ethylene .

Guseinov et al. [84] conducted a study using a pulse-method teqhnique ,also supports a Rideal-Eley type of mechanism where oxygen adsorbs on a reaction center of composition Ag_2O , either as a partially ionized molecule or as surface oxide of composition Ag_2O_2 . The electrophilic adsorbed molecular oxygen reacts with gaseous ethylene to form ethylene oxide while the Ag_2O_2 surface oxide is capable of rupturing or weakening the C-H bond of ethylene to form total oxidation products (28). It appears that a mechanism based on adsorbed ethylene can also be concluded from such behavior and ,as

discussed below , the participation of adsorbed ethylene has been deduced from recent transient spectroscopic and tracer studies .

Infrared spectroscopy were employed by Force and Bell(66) to identify species present on the catayst surface under ethylene -oxidation reaction conditions . A completely different machanism was proposed in which O- ions adsorbed on the silver surface are primary oxidizing agents for both reactions . They proposed that ethylene participates in both gaseuos and adsorbed forms , the former yielding primarily carbon dioxide and water . They have also suggested that two complexes Ag-O-CH2-CH2 and Ag-O-CH-CH3 , function as intermediates in the formation of ethylene oxide and carbon dioxide , respectively . Cant and Hall's (93) in their investigation of the oxidation of labeled ethylene supports this mechanism as do the experiments of Larabee and Kuczkowski (94) related to stereospecific oxidation of ethylene studied by microwave specroscopy . In contrast , Korchak et al . (95) ,from a static study at temperatures from 403 to 533 K , proposed that the complex Ag-O-CH2-CH2 is strongly bounded to the silver surface and is incapable of desorbing , but it isomerizes to acetaldehyde which rapidly oxidizes to carbon dioxide and water .

The inhibtion of the ethylene oxidation reaction by one or more of the oxidation products has been observed by many workers[3,66,8,11,36]. Hayes found that the partial oxidation reaction is inhibited by carbon dioxide , but the complete oxidation reaction is not affected by it . Contradictory results are reported by Mikami et

al.[81] who suggest that carbon dioxide is preferentially adsorbed on the most strongly adsorbed oxygen , threby inhibiting the formation of carbon dioxide and water and , correspondingly , increasing the selectivity of the reaction . Nault et al.[66] found that both reactions are inhibited by carbon dioxide .Many workers [3,66,8,11] have proposed rate eqution in which they have considered such inhibition by the reaction products.

A range of activiation energies for the partial and the complete oxidation of ethylene over silver catalysts has been reported by many workers . The wide range variations in these results can probably be attributed to the fact that some of the catalysts used in the investigtions were intentionlly or unintentionlly promoted or that in some cases the reactions might have been diffusion limited . Table-3 sumarizes some of the values for the activiation energies reported .

2.5 *Catalyst studies*

Silver is the only applied catalyst for the selective oxidation of ethylene to ethylene oxide with the production of carbon dioxide and water as by-products.Several patents describe methods of preparation of such silver catalysts for the oxidation of ethylene . In contrast with the great technical and economic importance of its application , only a reltively small amount of published scientific work has been focused on the catalysts themselves.

Silver has been used as a catalyst in the follwing forms : masive metal ,evaporated films , powders , silver alloys ,and supported on nonmetalic carriers . The last form is the most often studied scientifically and applied in industrial use .

Many types of materials have been used as supports , all of relatively low surface areas less than 1 m2/g . According to several reviews high surface area supports result in catalysts which exhibit unsatisfactory low selectivities . The most frequently encountered carriers are silica , alumina , silica-alumina, and silcon carbide, but alpha -alumina is the most widely used support for silver . Of the many recipes in the patent literature for silver catalyst preparation , the most commonly cited method is impregnation of a support from a silver salt solution , usually silver nitrate ,followed by hydrogen reduction and calcination .

Belaya and Rubanic [85] studied how conditions used in the preparation of pure , unsupported silver catalysts affected their specific activity in the oxidation of ethylene . They concluded that pure silver , regardless of the method by which it is prepared , always has about the same specific activity . They showed that variations in activity are mainly due to variations in the low concentrations of chloride ions present in the catalyst . The same conclusion cannot be extended to supported silver catalysts because of many different phenomena(such as support-metal interactions) which can be caused by the presence of the support.

Studies of the effects of the carrier on the activity and selectivity of supported silver catalysts for the oxidation of ethylene have been conducted by Riassian et al. [85] . The former authors used alumina and silicas of moderate to high surface areas and measured very low selectivities for catalysts supported on activiated alumina or silica gel. Although , in general, alumina-supported catalysts seem to be more active ,no tentative conclusion can be drawn from this study concerning the performance of each support because of the many variables which were left uncontrolled , most importantly the total surface area , the size distribution of silver crystallites , and the effectiveness factor. The result suggest that a possible influence of metal-support interactions on the performance of the catalyst .

Riassian et al.[86] investigated the infuence of the support on the catalytic activity and selectivity of silver deposited on silica , alumina ,and glass . Significant differences in activity and selectivity (see Fig.10)depending on the nature of the support were observed . The authors attributed such differences to impurities originating from the support and from the adsorption of organic material on the surface of the catalyst .Their study ,done under ethylene oxidation conditions , showed that the nature of the support has a pronounced effect on the rate of sintering of supported silver . This effect was attributed to both the surface energy of the support and to impurities from the support which diffuse to the surface of silver .

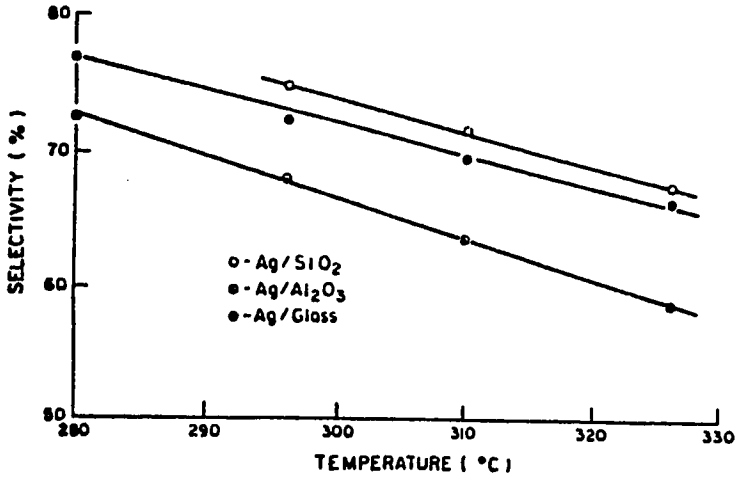


Figure 10. Effects of the support on selectivity. After Riassian et al. [86].

Other studies(86,87) of the sintering of silver catalysts under ethylene oxidation coditions have shown that silver migration involves surface diffusion and that reorganization of the metal is accelerated in the presence of oxygen and of chlorine .

The first investigators to consider the effects of crystallite size of supported silver catalysts were Presland et al. [87] .During the sintering of evaporated silver films they observed changes in catalytic activity related to the reorganization of the metal when the catalyst was exposed to oxygen at the temperature of the reaction . Wu and Harriott (96) have reported what appears to be the only systematic study of the effects of crystallite size on the activity and selectivity of silver catalysts . Using catalysts with average crystallites between 20 and 500 Å obtained by sintering , they found that activities per unit silver surface area for both ethylene oxide and carbone dioxide formation decreased with increasing crystallite size . The selectivity for ethylene oxide was nearly zero and gradualy increased to 60% for 500 Å particles . Recent experiments indicate a reversal trend for particles larger than 500 Å .

The effects of crystallographic orientation on the activity and selectivity of silver catalysts have also been investigated by some authors . Orzechowski and MacCormak [8] were the first to propose such effects; who measured rates and attributed the differences in the values of the rate constants to be effected from different crystalplanes . Their additional suggestion that the activity and selectivity of the catalyst could be affected by the preferential poisoning of only some

of the silver planes is the same as stating that different planes exhibit different activity and or selectivity in the oxidation of ethylene.

Kummer[88] tried to determine the effects of crystallograghic orientation on the rates of the partial and complete oxidation of ethylene using single crystals of silver, but observed no difference in the activity of the different faces. It was later shown, however that under reaction conditions silver films rapidly recrystallize to a random orientation. The latter investigation attempted to determine the effects of crystallographic orientation by conducting the reaction on randomly oriented silver films and on oriented films with the crystal plane prefrentially exposed (28). They observed no differences in catalytic activity or selectivity, but the significance of this result is reduced by their low-angle electron diffraction study which showed that the film lost its orientation when exposed to reaction conditions(28).

Woodward and co-workers(97) conducted a similar investigation using single crystal of silver with a single crystal plane exposed produced a similar conclusion that crystal orientation has no effect on the reaction rates. These authors also studied the effects of dislocations on the activity of the catalyst and concluded that dislocations do not act as active sites for the oxidation of ethylene. An increase of silver dislocation will result in a decrease in oxidation rates. This is because oxygen binding increases at the dilocations of

silver . This increased binding of oxygen will result in blocking surface sites .

The uniqueness of silver as a catalyst for the partial osxidation of ethylene was recently related to exo-electron emission by Sato and Seo[89] .They found that a chemically stimulated exo-electron emission occurs continuously from silver catalysts during the partial oxidation of ethylene . This phenomenon was viewed as thermoelectron emisson from a thin semi-conducting oxide layer on silver , the work function of which is reduced by adsorption of ethylene in the form of ethylene oxide . No exo-electron emission was observed when ethylene -oxygen mixtures were brought in contact with metallic copper , nickel oxide , and iron oxide , all of which exhibit no catalytic activity for ethylene oxide formation , but only complete oxidation of ethylene (28).

Little has been reported For the use of silver in alloy form to selectively oxidized ethylene. Fank and Beachell (67)studied the oxidation of ethylene over silver-gold alloys and concluded that overall activity for ethylene oxidation is dependent on lattice spacing .This conclusion must be regarded as tentative because other possible effects of the silver-gold alloy system could not be excluded ,e.g. , an alteration of the electronic interaction. These workers also showed that gold , at low concentrations in the silver , acts as a promoter for ethylene oxide formation. Their dymamic adsorption data indicate that the catalytic activity is related to surface sites having fairly low

adsorption energies since strong sites bind the oxygen too firmly to permit a high reaction rate . This conclusion agrees with results of Woodwardet al. [97] and Moss et al. (98) who oxidized ethylene over palladium-silver alloy films and obtained the highest ethylene oxide yield over pure silver decreasing to zero over alloy films with 40% palladium or greater . The higher activity of palladium-silver alloys for the complete oxidation reaction was correlated with a lower heat of oxygen chemisorption . Identical results were obtained by Cormack et al.[99] using supported silver -palladium alloy catalysts .

Silver catalysts for the oxidation of ethylene modified by the inclusion of additives have been described in a number of publications including patents . It is generally agreed that the maximum activity or selectivity occurs when the surface of the catalyst is only partly covered by the additives Whereas higher coverages seem to poison the catalyst . Such additives are either added directly to the catalyst or to the gas feed stream during the course of the reaction(28)

It is known that the addition of chloride ions to the catalyst or the addition of trace quantities of chlorine or halogenated organic compounds in the feed stream considerably improves the selectivity of the reaction [43] . From oxygen adsorption studies on silver in the presence of chlorine,Kilty et al. (91)concluded that the effect of chlorine is to inhibit dissociative adsorption of oxygen . According to their viewpoint , this inhibition increases the selectivity because they accept the argument that adsorbed molecular oxygen is responsible for

the selective oxidation of ethylene to ethylene oxide .

Ostrvskii et al. [20] studied the effects of Sulfur , Selenium ,Tellurium , and Chlorine additive to silver catalyst at concentrations in the range of 10^{-5} to 10^{-1} atom% . Sulfur ,chlorine , and selenium , in small concentrations increased the overall activity of the catalyst severalfold , although the effect of tellurium was very small (see Figure 11) . At higher concentrations , those additives decreased the overall catalytic activity but increased selectivity . The changes in catalytic activity and selectivity were explained as resulting from changes in the bond energies of the adsorbed oxygen brought about by the additives . An identical effect of selenium is also reported in (100). But in recent study , Kul'kova et al. [45] , using a radioactive isotope of selenium , showed that selnious acid and not elemental selenium is responsible for the catalyic promotion .

Margolis and co-workers [75] in a more fundamental effort showed that the effect of such additives is to change the electronic work function of silver . Substances which are electropositive relative to silver decreases the work function of the catalyst and in turn decreases the selectivity for ethylene oxide formation . The work of Wilson et al. (101) supports the above argument by showing that Phosphorus , Sulfur , and Chlorine causes the surface potential of silver to become more negative . Yet, another explanation is proposed by Force and Bell (66) who observed a reduction in the overall oxidation rate and an increase in selectivity after their silver

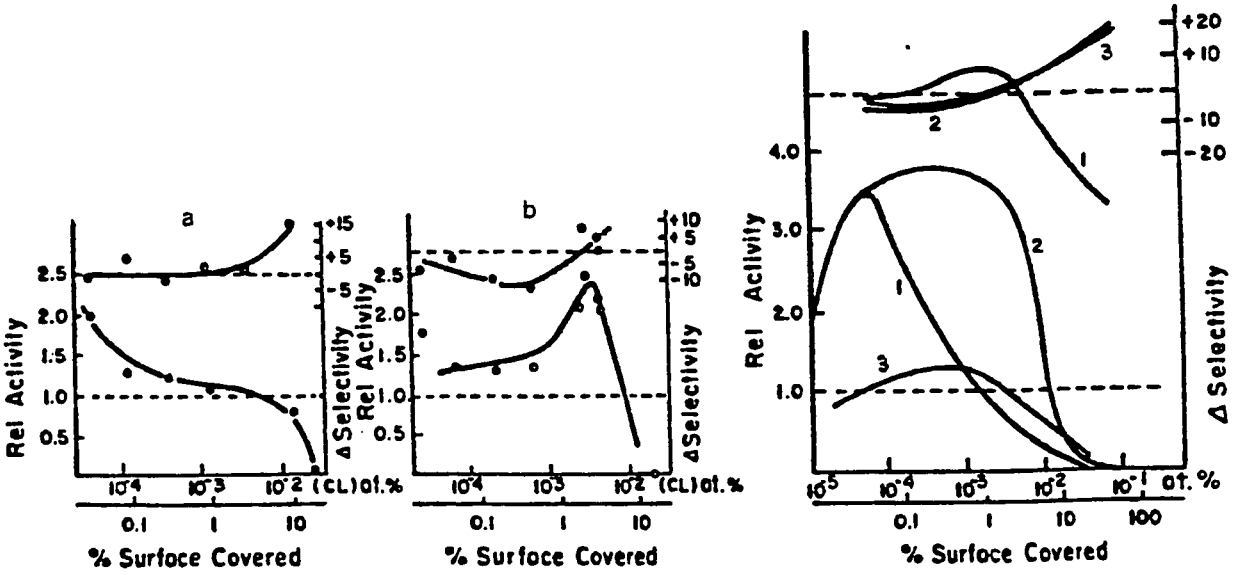


Figure 11. Dependence of catalyst activity and selectivity on additive concentration. (a and b): Chlorine under different conditions.(1) Sulfur, (2) selenium, and (3) tellurium. After Ostrovaskii et al. [44]

catalyst was exposed to dichloroethane . The effect of such moderation was considered to result in a reduction of the rate of chemisorption of both ethylene and oxygen in the presence of chloride ions , as well as enhancement of the adsorption of the reaction products .

The role played by Calcium and Barium additives to silver catalysts for the oxidation of ethylene is debated . Forzatti et al. (102) report that the addition of Barium or Calcium influences only the activity . The increase in the activity of the catalysts promoted by BaO2 or BaCO3 is attributed by Spath et al. (103) to stabilization of the catalyst matrix and to coverage of the silver matrix with a semiconducting film containing silver atoms as donors of electrons , thereby decreasing the work function of the the catalyst matrix .

Carberry et al. (104) and forzatti et al. (102) showed that preirradiation by ^{60}Co γ-rays caused an increase in the activity of supported silver for ethylene oxide formation without altering its activity for formation of carbon dioxide and water , thus increasing the selectivity of the catalyst . Although the catalyst was restored to its original activity and selectivity after hydrogen reduction and reoxidation in air , re-irradation of the irraddiated -reduced -reoxidized catalyst reproduced the same effects . The authors attributed the increase in activity and selectivity of the irradiated catalysts to the migration of calcium impurities from the bulk crystals of supported silver to the catalyst by electron spectroscopy (ESCA) . These authors also assumed that ethylene oxide formation

proceeds via adsorbed molecular oxygen , O^{2-} , whereas the complete oxidation reaction proceeds via an adsorbed atomic oxygen , O^{-} . They recognized the ability of calcium to form superoxide and attribted the increase in selectivity upon irradiation to surface calcium which increased the ratio of the superoxide O^{2-} to peroxide O^{-} . It is interesting to note that calcium was not detected at the catalyst surface either before the irradiation or after the reduction of the irradiated catalyst(28) . Calcium was detected (by ESCAO), however , after the initial irradiation and after the reduction re-irradiation cycle .

The assumed role of surface calcium on supported silver catalysts was later verified by Forzatti et al. (102) and by Carberry et al. (104) who intentionally added Ca to the catalyst .The results obtained upon irradiation of this catalyst were the same as those obtained upon earlier (28) ,verifying that surface calcium is indeed responsible for the increased activity and selectivity of γ-irradiated catalysts . An SEM study of γ-irradiation catalysts exopsed to ethylene and oxygen at 553 K revealed spheroidization of the silver particles on the support , a phenomenon which was not observed in the absence of γ-irradiation .This phenomenon was attributed to ionization of an included Calcium oxide or hydroxide phase dispersed on the silver , thereby causing an energetic ejection of the Ca to the surface of silver resulting in observed spheroidization of the silver particles .

It has also been observed that amines retard the oxidation of

ethylene over silver . Inui and Tanabe (105) reported selective inhibtion of the complete oxidation reaction by amines on cataysts with high combustion activity ; and a nonselective inhibition of both reactions on catalysts with higher activity for ethylene oxide formation .

The imprtance of the pretreatment and recent history of the catalyst has been recognized by many authors . Nault et al. [66] first studied the effects of pretreatment on activity and selectivity . They exposed the catalyst overnight to pure oxygen at 473 K and then pretreated it with ethylene . After an initial surge of product formation , the activity fell slowly , leveling off after 2 hr. When the catalyst was reduced in hydrogen , however , and then treated with ethylene , it was more active than the one pretreated with oxygen . The oxygen - pretreated catalyst showed an initial reduction in activity followed by a gradual rise ,whereas a catalyst pretreated with hydrogen behaved conversely . Very high activity , increasing during the first 30 min of the reaction , was observed for a catalyst which was pretreated with ethylene oxide . The main conclusions fron these pretreatment studies are that the catalyic sites are at least partially reduced and that the pretrearment with ethylene oxide either produced new sites or increased the activity of the existing ones .

chapter 3

EXPERIMENTAL INVESTIGATION

3.1 *Experimental equipment*. The equipment is divided into the following (Figure 12.):

1) Feed metering system
2) High pressure reactor system
3) control box
4) Power supply
5) Analytical section

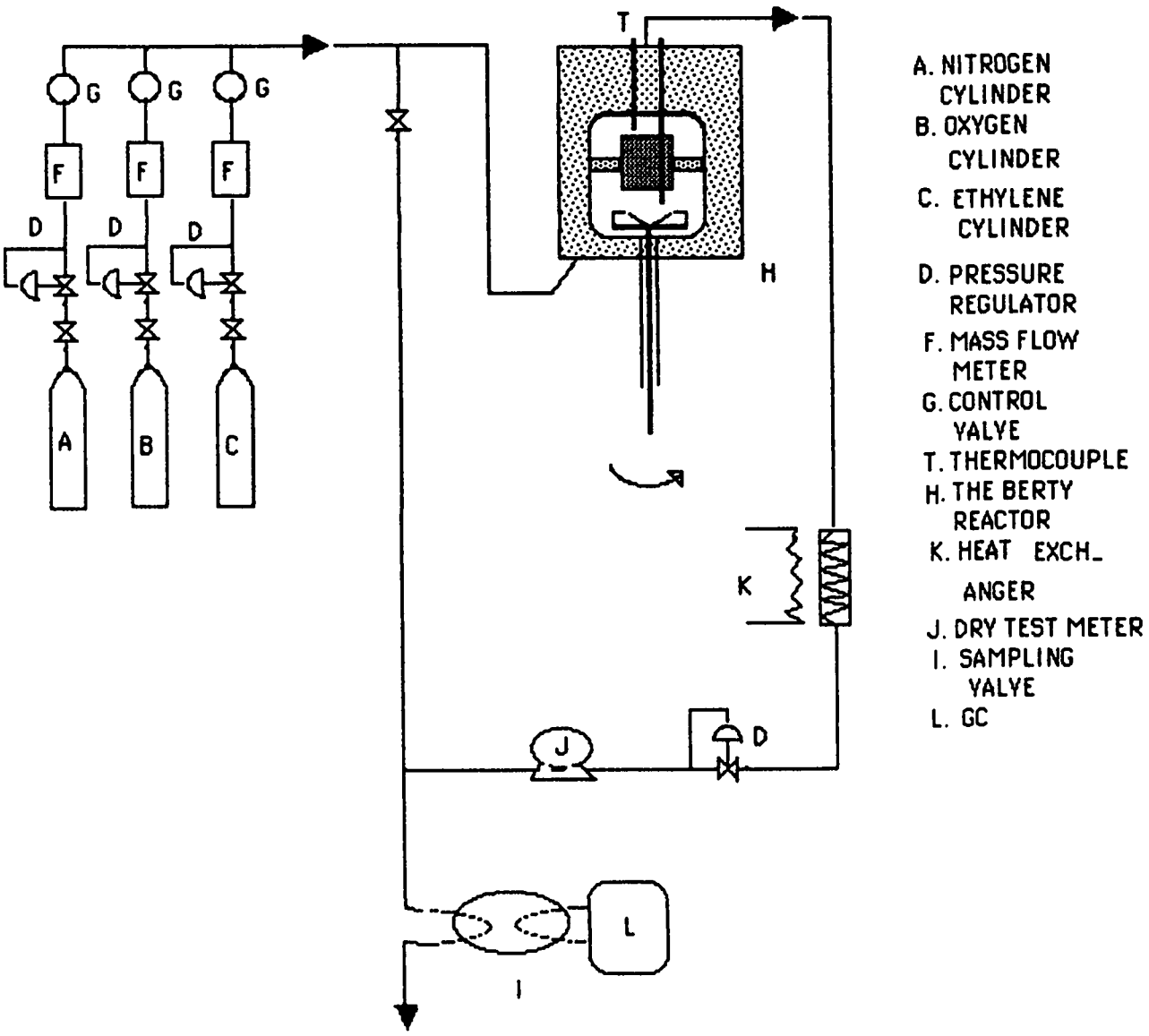


FIGURE 13 THE ETHYLENE OXIDATION UNIT FLOW-SHEET

3.1.1 *Feed metering system*

The feed metering system consists of three gases : compressed nitrogen , oxygen ,and ethylene (99.9%) . These gases are supplied in cylinders by Matheson Gas products,Inc.

Brook mass flow meters were used to control the desired inlet gas flow rate and composition .

The reaction product leaves the reactor and is water cooled . The water vapor is condensed and separated in a separator . The product then flows through a dry test meter and then to the exhaust . The down stream pressure in the system is maintained by a backward high pressure regulator.

A line branches out to the Perkin Elmer gas Chromatograph for analysing the inlet gases .

3.1.2 *High pressure reactor system*

The high pressure reactor system (as shown in Figure 13.) includes gas feed equipment , Berty catalytic reactor , heat exchanger to cool the product , product separator , and product discharge equipment .

The reactor was designed by Berty of Union Carbide and built and supplied by Autoclave Engineers ,Inc. The design of the reactor is shown

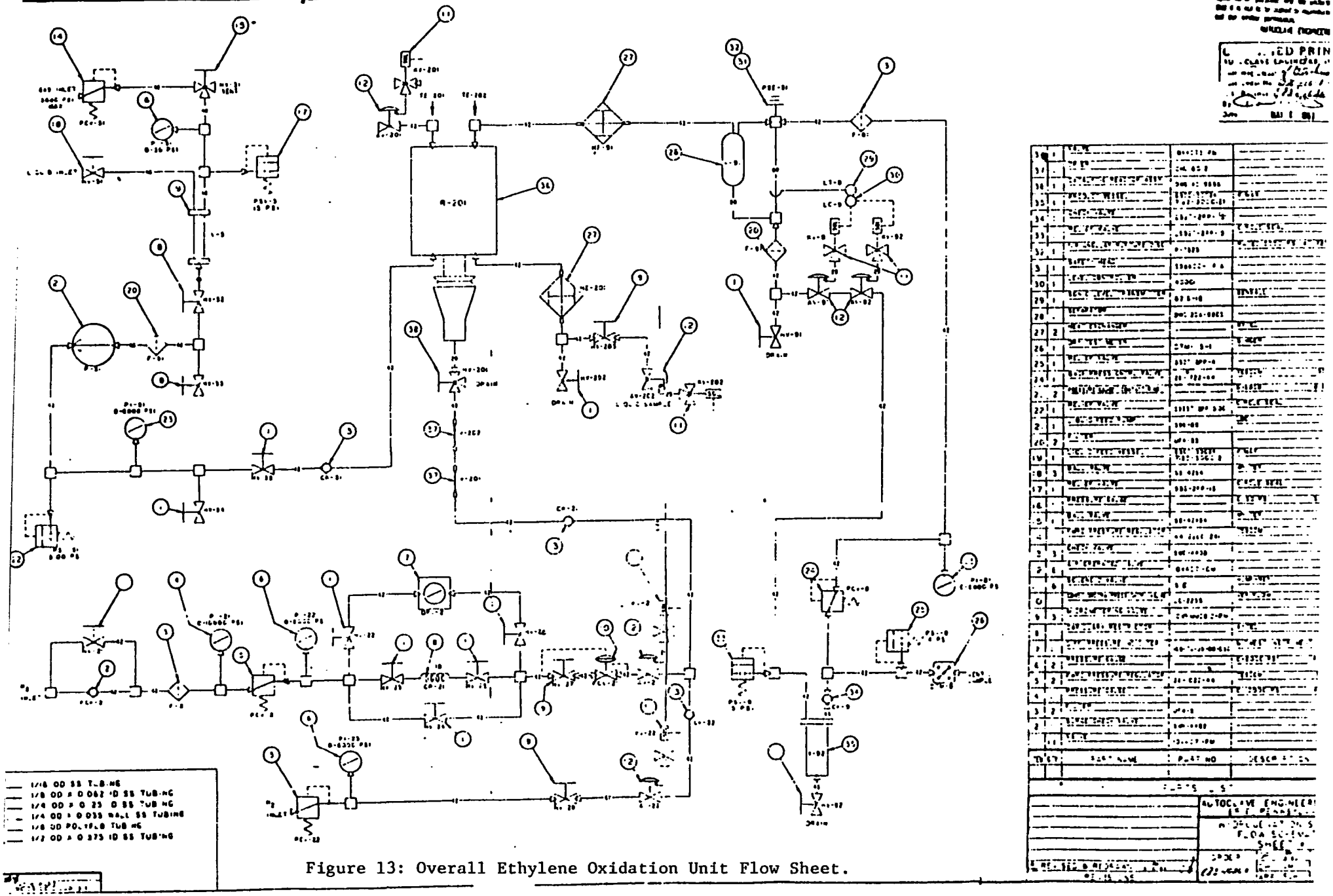


Figure 13: Overall Ethylene Oxidation Unit Flow Sheet.

in Figure 14. This gradientless CSTCR can be described as made up of the following main parts :

1. The body and cover assembly which can be used up to a maximum allowable pressure of 5800 psi at 616 K. This temperature limitation is due to the teflon bearings used in the magnadrive assembly . however , the operating temperature limitation can be increased to 866 K by the use of purebon or vulon bearings with a water -cooled jacket between the magedrive and the reactor . the cover is provided with two connection to introduce a pencil type thermocouple to the top and to the bottom of the catalyst bed . The lower thermocouple is connected to an PID temperature controller ,which maintain the temperature .

2. The agitation assembly is designed for a maximum allowable pressure of 5800 psi and is run by a 1/4 horsepower d-c motor . The maximum allowable rpm is 1500 . The assembly is especially designed to eliminate leakage and packing heat generation . In general, high speed rotary agitation is effected by the rotation of external magnets which actuate internal magnets fastenened to the shaft . A d-c motor rotates and controls the rpm of outer magnet drive with the help of a solid-state silicon rectifier- controller .

3. The furnace is divided into three heating zones , top zone , middle zone and bottom zone .

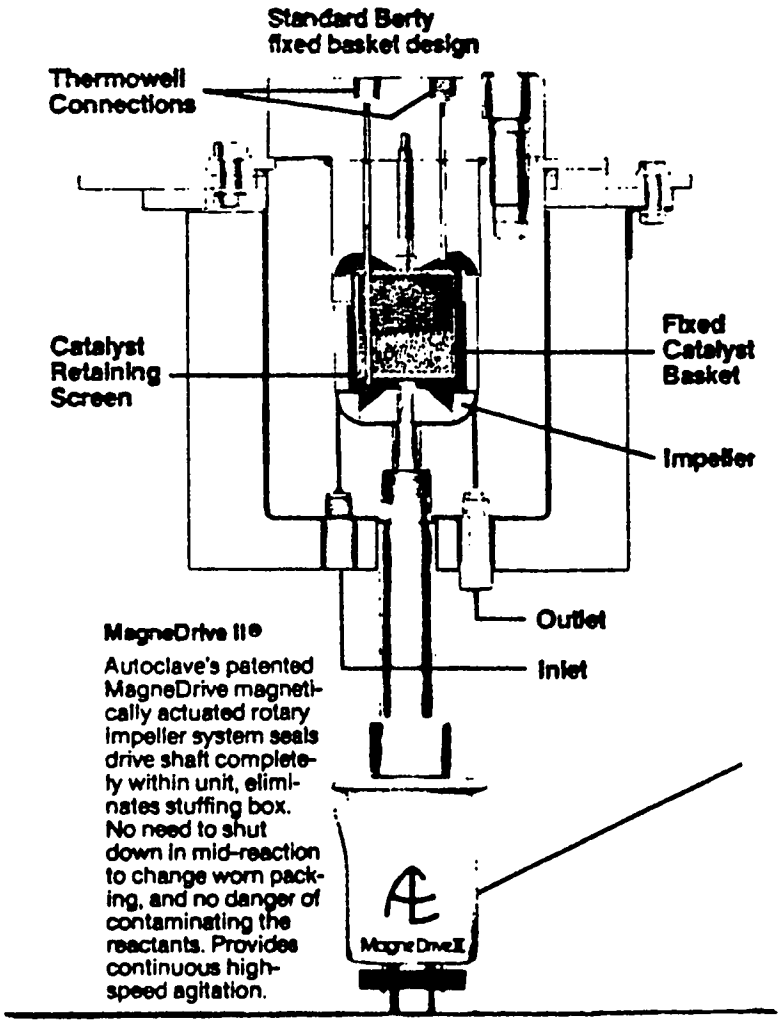


Figure 14 Berty reactor

4. The catalyst basket can hold up to 100 cm^3 of catalyst .The catalyst used in this work filled around one third of the total volume of the basket .

3.1.3 *Control box*

The control box has the following functions :

1- Motor speed controller with digital tachometer.

2- Three ammeters to control and indicate the current load to each of the furnace zones .

4-Temperature digital indicating controller to indicate the temperature of the reactor . This is a proportional integral derivative controller . Also, there are three other temperature digital indicators to indicate the temperature of the three zones of the furnace .

5-Buttons to open and close the air operated valves .

6-Audible warning system in case of unaccounted temperature rise

7-Emergency shut down bottons where it close all gases and open the nitrogen purging line .

3.1.4 *Power supply*

Power is supplied by six independent 120-volt lines . One line supplies the power to the control box . Three lines supply power to the three zones of the reactor furnace . Power to the gas chromatograph

and the data console is supplied by two independent 120-volt lines.

3.2 *Analytical section*

Both the inlet and the product streams are continuously analyzed by a gas chromatograph through an automatic sampling loop of 10 cc. The gas chromatograph which can be temperature programmed is Perken Elemer attached to a data consol . The columns used are 6-foot chromosorb 102-100/80 mesh size in series with 12-foot chromosorb 102-80/60 mesh size.

3.3 *Materials*

The catalyst used in this investigation is supplied by Harshaw/Filtrol partenership . The pellets are 1/8 x 1/8 in. cylinders . THe catalyst support is α -alumina . A typical analysis is shown in table -4

Table -4 A typical catalyst analysis

total leachable Ag	7.96%
H2O soluble	less than 0.01%
Fe	8.8 ppm
Cl	3.4 ppm
S	1.3 ppm

3.4 *Experimental procedures*

The reactor was loaded with 63 gm . of 8% Ag. To do this , the two thermocouples which are fitted through the cover are dissconnected and very carefully pulled up . Any bending will break the thermocouples ;then the catalytic basket is taken out and filled with required amount of catalyst . After doing so ., the basket is returned and it should be positioned in the same manner as before so that the longer thermocouple case inside the basket will match with the opening in the cover . This is to allow for the longer thermocouple to go through and to the bottom of the catalyst basket .Then , the heavy cover is closed in a manner shown in the reactor catalog , Also, the insulation cap can be mounted on the cover . After this the two thermocouples are connected . Then the system was pressurised with nitrogen from the nitrogen purging line to 800 psia to check for any leak . A routine run was carried out by the following procedures :

1- Connect the Brook flow meters to the power supply ,then Warm for at least 15 minutes .

2-Open the feed line to the chromatograph , close the feed line to the reactor , adjust the Brook flow meters to the desired readings , then get the inlet composition by GC. ,close the Brook flow meters .

3- Open the reactants line ,close the nitrogen purging line ,adjust the backward pressure regulator to the desired pressure (300 psig) .

4- Open the feed line to the reactor ,Close the feed line to the GC , introduce nitrogen to the system by the Brook flow meters , begine pressurizing the system.

5-Set on the reactor temperature by the temperature controller (the proportional , integral , and the derrivative constants of the controller were all set in former experimental runs) .

6-Set on the desired RPM.

7-When the temperature stablised at the desired level (about 1 C), oxygen was allowed in at the desired level , then ethylene is introduced at the desired level.

8-To analyze the product composition ,part of the product passes through a branching loop from the outlet pipe and fed to the GC through an automatic sampling loop.A sample chromatogram is included in the appendix A.

chapter 4

RESULTS

4.1 *General*

The parallel reactions to be experimently investigated are the partial oxidation of ethylene to ethylene oxide and the complete oxidation of ethylene to carbone dioxide and water . The reactor employed in these experiments is the Berty reactor which is a CSTCR with internal recycling . In addition to the advantages that a CSTCR can provide , such as ease of interpretation of data , internal recycling provides such high mass velocities that elimenate any of the physical resistances around the catalyst bed . Flow rate and temperature were the main variables where three temperatures have been chosen at 513 ,533, and 553 K . Pressure was kept constant at 300 psig . Also , the weight of the catalyst was kept constant at 63 gram . Since the reactor is a CSTCR , reacrion rates were calculated by simply

$$r_{C2H4} = F_A X / W$$

x is the conversion

F_A is the inlet moles of Ethylene

w is the weight of the catalyst

defining X1, X2 as the conversions of ethylene to ethylene oxide and carbon dioxide respectively ,then

$r_{C2H4-C2H40} = F_A X1 / W$ (1)

$r_{C2H4-C02} = F_A X_2 / W$ (2)

conversions were defined as

$X1 = (C_2H_4O)/[(C_2H_4)_{inlet}]$

$X2 = 0.5(CO_2)/[(C_2H_4)_{inlet}]$

selectivity is defined as $(C_2H_4)/ (C_2H_4+0.5*(CO_2)]*100$

The test started with a fresh catalyst and deactivation test was done to ensure the stability of the catalyst . Also , a number of runs were taken at three different RPM to examine the absence of the physical transfer limitations around the pellet . Special attention is paid to the selectivity since it is an imprtant matter .

4.2 *Experimental results*

4.2.1 *Gas chromatograph calibration*

In all experimental runs only ethylene oxide , carbone dioxide , and water were detected as reaction products . No other organic compound was detected . Table 5 shows the chromatograph conditions employed .Compounds elluded in the following order : nitrogen , oxygen

Table-5 gas chromatograph operating conditions

Chromatograph	Perkin Elmer
integrator	Perkin Elmer
columns	chromosorbe 102(6ft-80/60 mesh size)-chromosorb102(12 ft-80/100 mesh size)in series
column temp.	2 min's at 34 C , then up to 120 C at 25 C /min , hold at 120 C for 9 minutes
detector temp.	140 C
injector temp.	100 C
gas supply	helium, 40 cc/min.

, carbon dioxide, ethylene , and ethylene oxide.All compounds were identified by their retention times where previously each compound had been injected at the same chromatograph conditions and its retention time was identified , table -6 shows the sequence of the compounds elusion and their retention times .For calibration , pure samples of each material were used . Table-7 shows the responce factores obtained from calibration to correct the peak areas obtained from the chromatograph.. All the experimental results obtained are represented in the appendix d .

4.2.2 *Reproducibility*

The reproducibility of the data was tested by repeating a number of runs at identical conditions , and it was found to be reasonably reproducible . No initial activity increase was observed except with the fresh catalyst . Table -8 and Figure15 shows these reproduced runs .

4.2.3 *Deactiviation*

Figure 15 shows the results obtained for the deactiviation test where reaction rates are plotted vs time . The temperature of the reaction was 533 K. This plot shows that the rate of conversion of ethylene to ethylene oxide increased quickly during the first five houres while the rate of conversion of ethylene to carbon dioxide decreased rapidly at the first two houres . Approximately after seven

Table-6 retention times for each compound

COMPOUND	TIME
NITROGEN	78 sec.
OXYGEN	89 sec.
CARBON DIOXIDE	3.49 min.
ETHYLENE	4.81 min.
ETHYLENE OXIDE	13.51 min.

Table -7 responce factores obtained from calibration

compound	responce factor
nitrogen	1.000
oxygen	1.076
carbon dioxide	0.8309
ethylene	0.8109
ethylene oxide	0.7042

Table-8 Reproducebility data

Run#		T(K)	Q(l/hr)	r*	r rep.
9-10	CO2	533	25.4	14.6 E-5	14.8 E-5
9-10	EO	533	25.4	21.9 E-5	21.3 E-5
17-19	CO2	513	9.25	5.69E-5	5.66E-5
17-19	EO	513	9.25	6.08E-5	5.95E-5
22-27	CO2	553	9.25	1.27E-4	1.25E-4
22-27	EO	553	9.25	7.37E-5	7.24E-5

* r is the rate of conversion of ethylene to each of ethylene oxide and carbon dioxide .

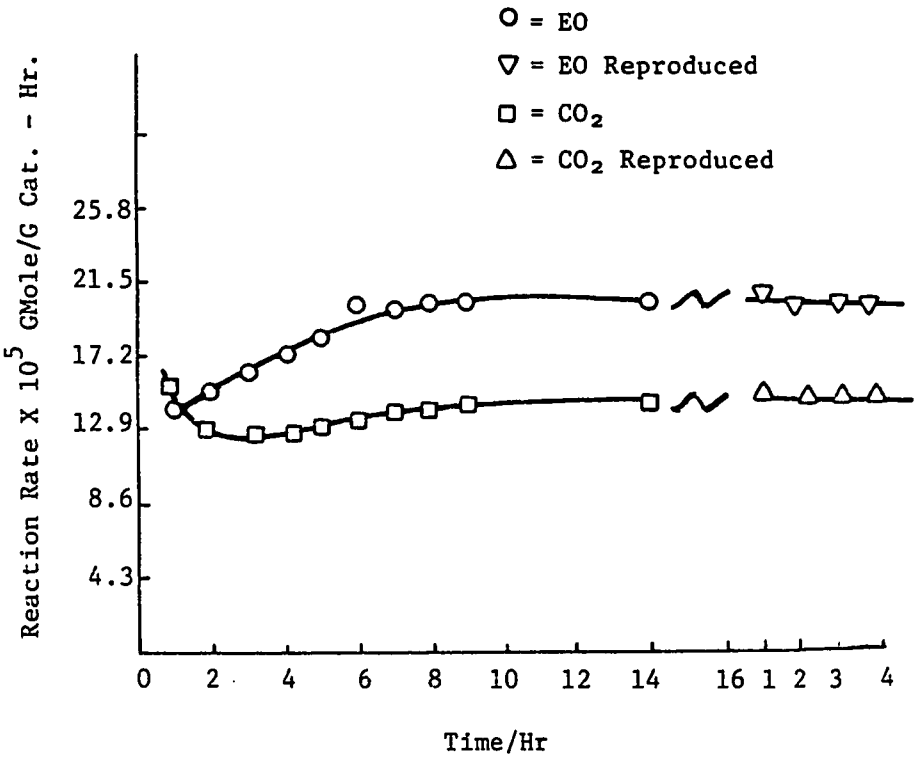


Figure 15: Initial Reaction Rates Vs Time
Fresh (Catalyst)

houres both reactions went steady . Similar behaviar has been cited in the literature [86] . Figure(15) also shows the reproduced runs . These runs were taken after the reactor has been shut down and brought to operation a gain . The purpose of reproducing these runs is that to ensure the stability of the catalyst and the initial activity increase was not taking place again .

4.2.4 Reaction rates vs RPM

Figure(16) shows a plot of reaction rates vs RPM at three temperatures , 553 K ,533 K , and 513 K. The range of RPM was from 350 to 950 RPM . These runs were conducted to examine the external physical transport resistances .

4.2.5 Temperature difference across the catalytic bed

There are two thermocouples to indicate the temperature of the catalytic bed . One thermocouple is located at the top of the catalytic bed ; the other is located at the bottom of the catalytic bed . This arrangement of thermocouples is useful in order to indicate whether the operation is isothermal or not . In this work , the observed temperature difference across the bed ranged between o.5 and 2 K indicating an isothemal operation .

4.2.6 Effect of conversion and temperature on selectivity

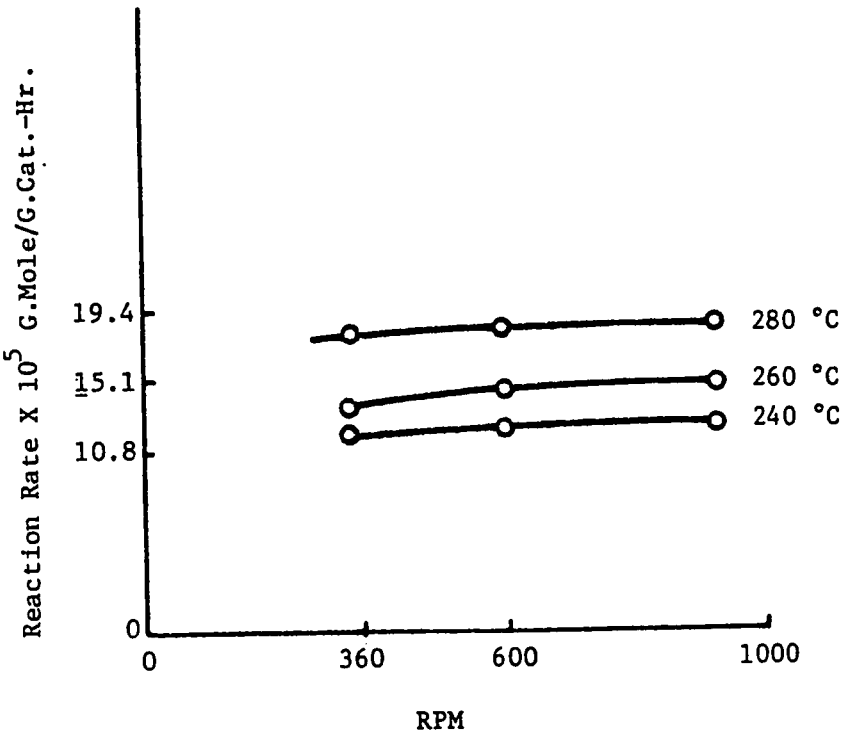


Figure 16: Reaction Rates Vs RPM

A plot of selectivity of ethylene oxide(moles of ethylene oxide formed per moles of ethylene reacted times 100) vs total conversion of ethylene to ethylene oxide and carbone dioxide at 513 , 533 , 553 K is shown in Figure(17). This plot shows that selectivity of ethylene oxide deceases with further increase in total conversion . Extrapolating to 0 conversion gives an ethylene oxide oxide selectivity of approximately 76-78% . These numbers represent the highest selectivity that can be obtained by the catalyst . The effect of temperature is also shown in Figure 19.

4.2.7 *Kinetic data*

Table-9 shows the actual kinetic runs which have been used to obtain the reaction rates expressions. The data were measured at different flow rates (different residence time) , and at three different temperatures (513 , 533 ,and 553 K).

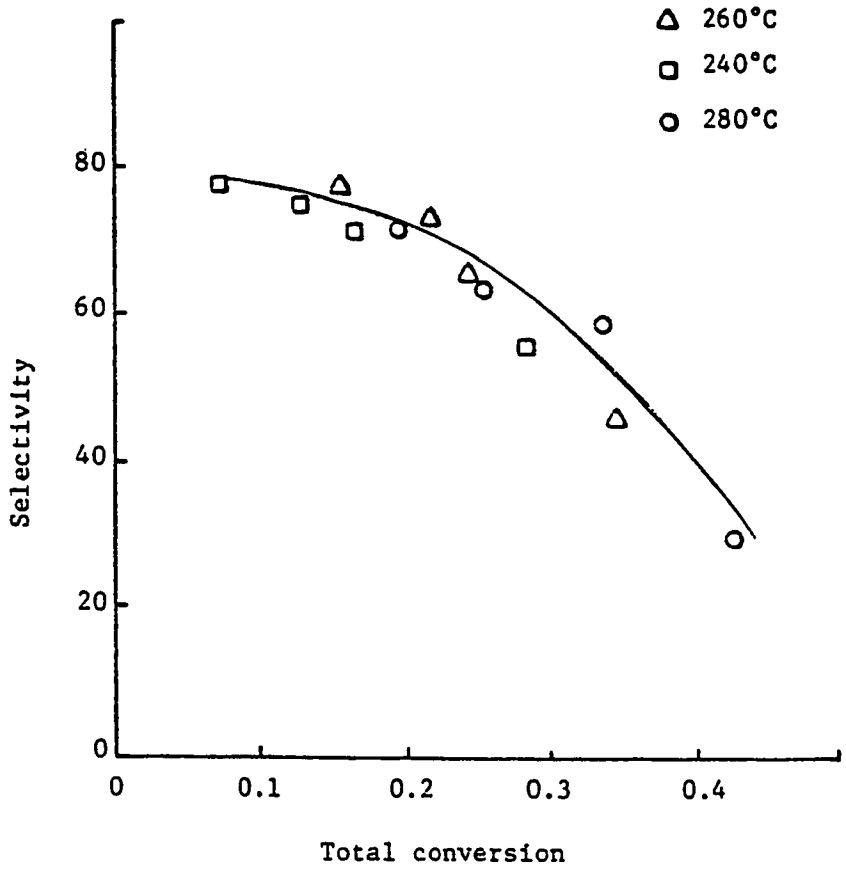


Figure 17: Selectivity Vs Total Conversion

Table-9 feed and product composition at various conditions

W= 63.25 g

P= 300 psig

RPM= 950

run#	T(K)	Q(L/Hr)	COMP.	INLET MOLE%	OUTLET MOLE%
23	553	9.25	N_2	74.71	74.83
			O_2	18.7	14.14
			CO_2	0.0	3.469
			C_2H_4	6.595	3.346
			C_2H_4O	0.0	0.7513
			H_2O	0.0	3.469
24	553	51.0	N_2	76.08	77.39
			O_2	19.52	16.32
			CO_2	0.0	1.247
			C_2H_4	4.40	2.918
			C_2H_4O	0.0	0.8793
			H_2O	0.0	1.247

run*	T(K)	Q(L/Hr)	COMP.	INLET MOLE%	OUTLET MOLE%
25	553	106	N_2	77.37	77.61
			O_2	18.89	17.48
			CO_2	0.0	0.7154
			C_2H_4	3.74	2.790
			C_2H_4O	0.0	0.6839
			H_2O	0.0	0.7154
26	553	275	N_2	78.15	78.50
			O_2	18.53	17.69
			CO_2	0.0	0.3683
			C_2H_4	3.33	2.589
			C_2H_4O	0.0	0.4831
			H_2O	0.0	0.3683
13	533	9.25	N_2	74.71	77.13
			O_2	18.7	14.01
			CO_2	0.0	2.117
			C_2H_4	6.595	3.706

run#	T(K)	Q(L/Hr)	COMP.	INLET MOLE%	OUTLET MOLE%
			C_2H_4O	0.0	0.918
			H_2O	0.0	2.117
14	533	51.0	N_2	76.08	77.19
			O_2	19.52	17.18
			CO_2	0.0	0.7681
			C_2H_4	4.40	3.358
			C_2H_4O	0.0	0.737
			H_2O	0.0	0.7681
15	533	106	N_2	77.37	77.74
			O_2	18.89	17.82
			CO_2	0.0	0.4249
			C_2H_4	3.74	2.972
			C_2H_4O	0.0	0.6165
			H_2O	0.0	0.4249
16	533	275	N_2	78.15	78.43

run*	T(K)	Q(L/Hr)	COMP.	INLET MOLE%	OUTLET MOLE%
			O_2	18.53	17.97
			CO_2	0.0	0.2282
			C_2H_4	3.33	2.729
			C_2H_4O	0.0	0.4145
			H_2O	0.0	0.2282
18	513	9.25	N_2	74.71	75.21
			O_2	18.70	16.33
			CO_2	0.0	1.548
			C_2H_4	6.595	4.377
			C_2H_4O	0.0	0.9864
			H_2O	0.0	1.548
28	513	51.0	N_2	76.08	77.06
			O_2	19.52	17.89
			CO_2	0.0	0.4222
			C_2H_4	4.40	3.662
			C_2H_4O	0.0	0.546

run*	T(K)	Q(L/Hr)	COMP.	INLET MOLE%	OUTLET MOLE%
			H_2O	0.0	0.4222
29	513	106	N_2	77.37	77.29
			O_2	18.89	18.5
			CO_2	0.0	0.2418
			C_2H_4	3.740	3.327
			C_2H_4O	0.0	0.384
			H_2O	0.0	0.2418
30	513	275	N_2	78.15	78.04
			O_2	18.53	18.50
			CO_2	0.0	0.1021
			C_2H_4	3.33	3.014
			C_2H_4O	0.0	0.1904
			H_2O	0.0	0.1021

chapter 5

DISCUSSION OF RESULTS

5.1 *Deactiviation*

At the start , wih a fresh catalyst , a deactiviation test was conducted .Reaction rates obtained were plotted in Figure15 . The temperature of the reaction was 533 K . This shows that rate of conversion of ethylene oxide increased fast during the first five houres while the rate of conversion to carbon dioxide decreased rapidly at the first two houres . Approximatelly after seven houres both reactions went steady . Figure 15 also shows reproduced reaction rates at the same reaction conditions . These reproduced runs were taken after interrupting the operation of the reactor . This indicates that the former fresh catalyst behavior does not repeat itself .

Such behviar has been cited in the literature , but no satisfactory explanation was given [86] .The explanation of such behavior is not direct since so many factors are interfering . However , one can say in general that a new active centres for ethylene oxide production could have been created . These centers are probably those who accommodate the species O^-. On the other hand , some of those active sites which are responsible for the production of carbon dioxide could have been blocked .

Reproduced results at the same conditions (temperature , composition , and flow rate) are shown in Figure 15 and it is found to be reproducible corresponding approximately to the steady state behavior of the catalyst.

5.2 *The effect of RPM*

The effect of RPM on reaction rates at different temperaturesis shown in figure 16. This shows that the reaction rates increased slightly with the increase in RPM . This indicates that external mass and heat transfer resistances are very small . This is further supported by using mass and heat transfer correlations where it is shown in appendix c that such resistances are minimal . It shoud be noted here that these correlations used for fixed beds can produce very reliable results since Reynolds is relatively large .

Many factors control the external mass and heat transfer , but Reynolds number had the main effect in reducing such external limitations . This is actually attributed to the high mass velocities provided by the impeller through the stationary catalyst bed .

5.3 *The effect of total conversion and temperature on selectivity of ethylene oxide*

Figure 17. shows the effect of total conversion of ethylene on

the selectivity of ethylene oxide at 553, 533 , and 513 K respectively . It is noticed that the increase of the total conversion of ethylene result in a decrease in the selectivty of ethylene oxide over carbon dioxide . This behavior is typical for parallel reactions with different orders , homogenious or hetrogenious . Also, it is noticed for such a system , that selectivity will go to a limiting value at zero conversion as it should be , where indeed, it is the case here with a limiting selectivity of approximatly 76-78%. The mechanism of Kilty (91) predicts a maximum selectivity of about 85.7% . The effect of temperature is also shown in figure 17 . The effect of total conversion of ethylene on selectivity is similar at the three indicated temperatures indicating the small effect of temperature on selectivity of ethylene oxide in the temperature range indicated .

5.4 *Kinetic modelling*

5.4.1 *Kinetic rate expressions*

In this work , a searching method was employed to find the best fit for the experimental data . Multiple linear least squares regression has been employed , but a strong emphasis was put on plotting and observing the trend at each of the three temperatures .Minimizing the number of constants was a strong objective .

The rate expression obtained are as the following

1) Rate of conversion of ethylene to ethylene oxide
(gmole /gcat.-hr):

$$r_1 = \frac{(1.354\times10^{3})\exp(-9010/T)(P_{O2})^{0.5}(P_{C2H4})^{0.6}}{1+(2.88\times10^{-2})\exp(2400/T)(P_{CO2})}$$

2) Rate of conversion of ethylene to carbon dioxide
(gmole/gcat.-hr) :

$$r_2 = \frac{(6.30\times10^{3})\exp(-10800/T)(P_{O2})^{0.5}(P_{C2H4})^{0.5}}{1+(1.57\times10\text{-}2)\exp(1530/T)(P_{CO2})}$$

In arriving to these equations , an emperical approach is basically employed . Assuming a mechanism was not a starting point . Reaction rates are found to be propotional to oxygen and ethylene pressures raised to indicated powers with carbon dioxide in the denominator where this is attributed to its inhibtion effects on the reaction Tables 10 and 11 show a list of reaction rates obtained vs f(c), the concentration function for ethylene oxide and carbon dioxide .

Table 10 Reaction rates of ethylene oxide vs f(c)*, the concentration function

T (K)	r (gmole/gcat-hr)	f(c)*
553	6.01e-5	1.14
553	3.16e-4	2.91
553	4.58e-4	4.70
553	8.15e-4	7.54
533	9.98e-5	1.62
533	2.62e-4	4.21
533	4.50e-4	6.45
533	5.71e-4	9.51
513	6.94e-5	2.12
513	1.97e-4	6.25
513	2.81e-4	9.10

*$f(c)=(P_{O2})^{.5}(P_{C2H4})^{.6}/[1+K_1(P_{CO2})]$

Table 11 Reaction rates of carbon dioxide vs $f(c)^*$, the concentration function

T (K)	r (gmole/gcat-hr)	$f(c)^*$
553	25.2e-5	5.72
553	44.8e-5	10.7
553	52.6e-5	13.6
553	62.4e-5	15.90
533	16.1e-5	7.89
533	27.2e-5	14.0
533	31.4e-5	16.20
533	38.6e-5	17.7
513	10.9e-5	10.4
513	15.2e-5	17.4
513	18.0e-5	19.2
513	17.6e-5	20.5

$^*f(c)=(P_{O2})^{.5}(P_{C2H4})^{.5}/[1+K_1(P_{CO2})]$

Figures 18. and 19. shows plots of reaction rates both of ethylene oxide and carbone dioxide vs the concentration functions f1(c), and f2(c) at various temperatures (553, 533, and 513 K). These plots shows that reaction rates are increasing with temperature as expected . Further more , these rate expressions found to fit fairly well the experimental data as shown in Figure (26) .

The network considered is a parallel one , since this is well established in the literature . Also , it is well established the consecutive oxidation of ethylene oxide is very small. At the present work , consecutive reaction is expected to be even extremely small bacause the catalyst is actully very well moderated with chlorine .

The models obtained proved to fit the experimental data well in the sence that experimental rates agreed well with the predicted rates . In literature , rate expersions for both the conversion of ethylene to ethylene oxide and carbon dioxide have many forms .The order of different species involved in the rate expression were varying considerably . Rate expressions based on mechanisms could not match the actual experimental data except with many constants, were probably any other mechanism would fit the data just as well .

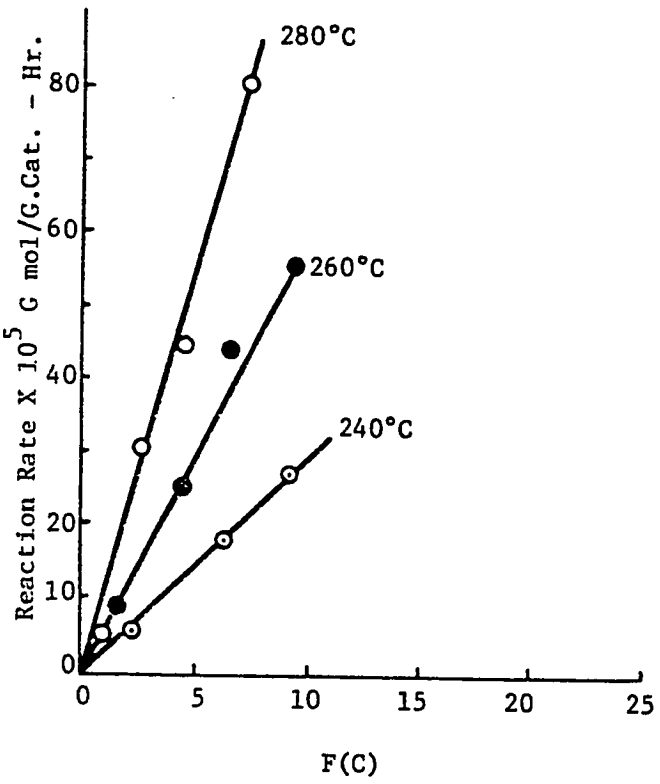


Figure 18: Reaction Rates Vs F(C)
for ethylene oxide

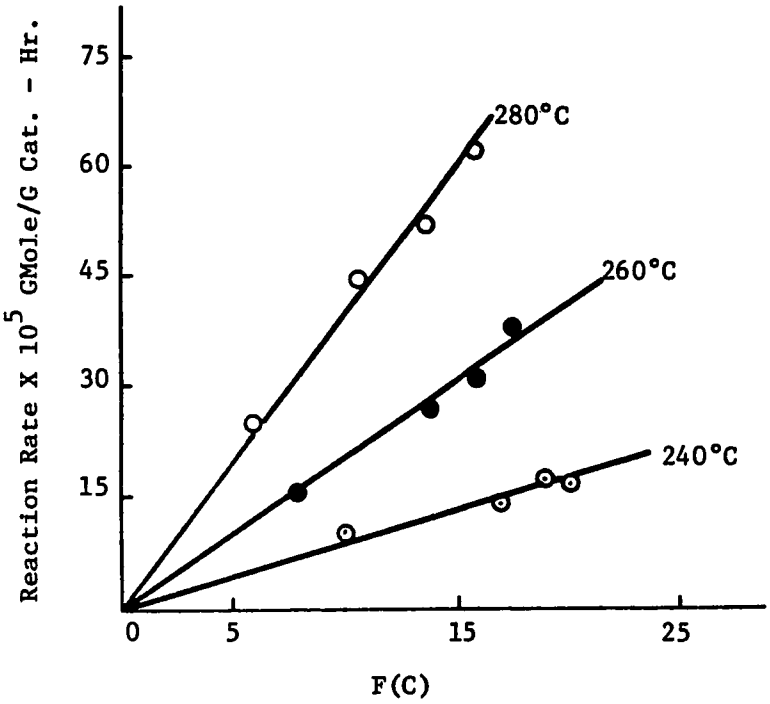


Figure 19: Reaction Rates Vs F(C)
For carbon dioxide

5.4.2 *Arrhenius plots*

Arrhenius plots of k and K1 for ethylene oxide and carbon dioxide are shown in figures 20, 21 ,22 ,and 23 . These figures show that activiation energies of both reactions are close to each other , while that for carbone dioxide are little different . This can be explained by the following

- Carbon dioxide is adsorbed on the two chemisorped peices of oxygen , diatomic and atomic where these two forms are responsible for the production of carbone dioxide and ethylene oxide .

Thus leading to two different binding energies or heat of adsorption which result in different inhibtion effects on both reactions (adsorption of ethylene and carbone dioxide on bare silver is weak , however with oxygen covered surface , adsorption is strong .

Table -10 shows reported activation energies together with the activation energies obtained in this work . Although it is difficult to compare results of different catalyst forms , the present work activation energies are among the highest . This could be an indication for the negligible mass and heat resistances .

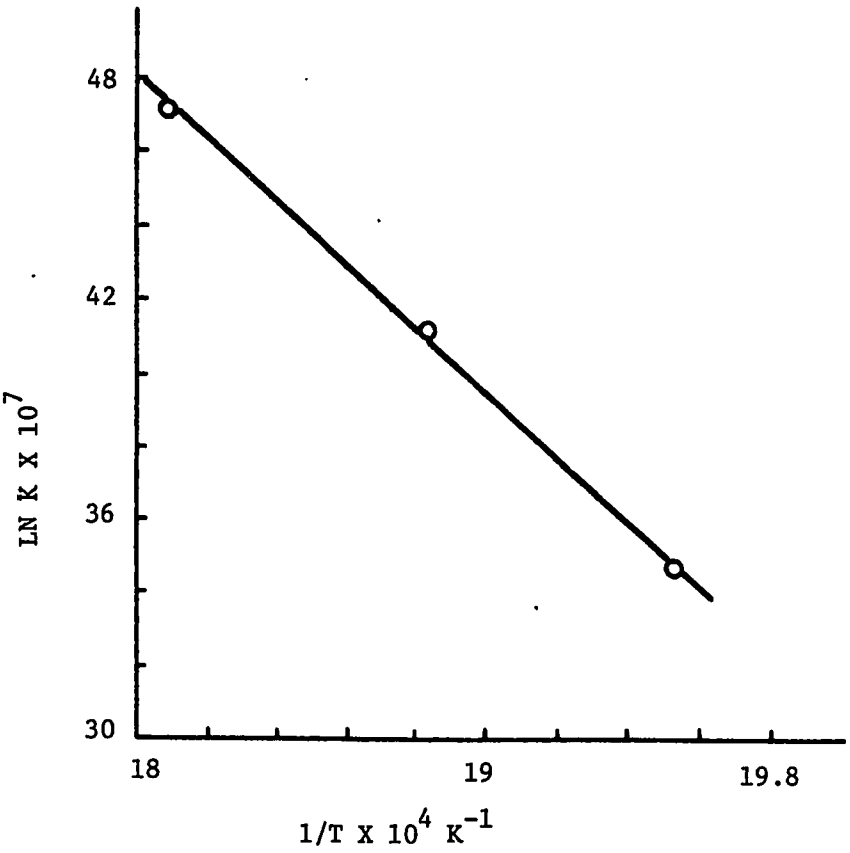


Figure 20: LN K Vs 1/T for ethylene oxide

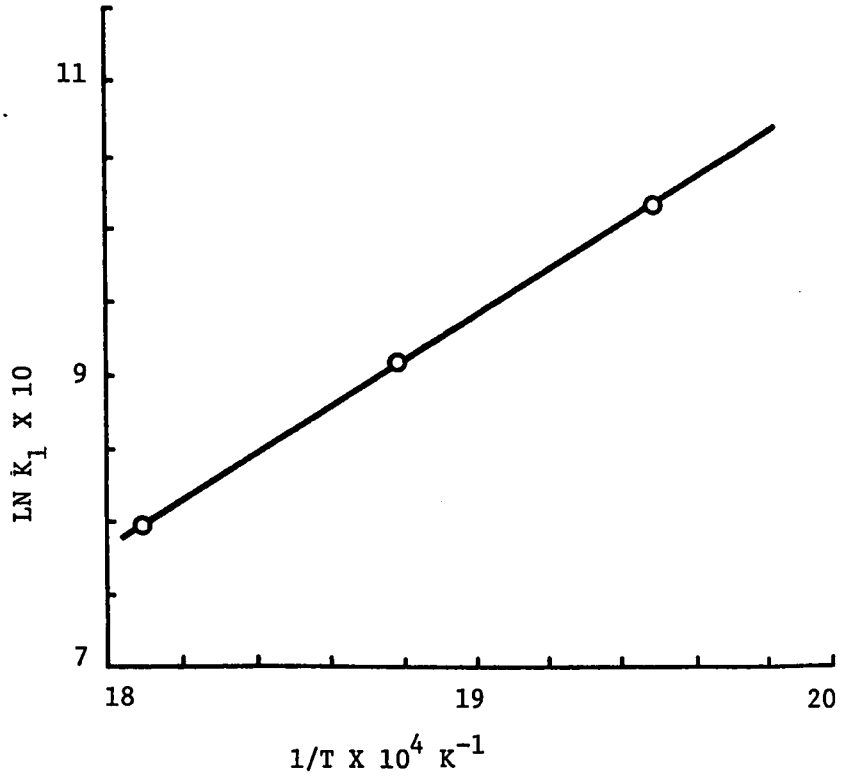


Figure 21: LN K_1 Vs 1/T for ethylene oxide

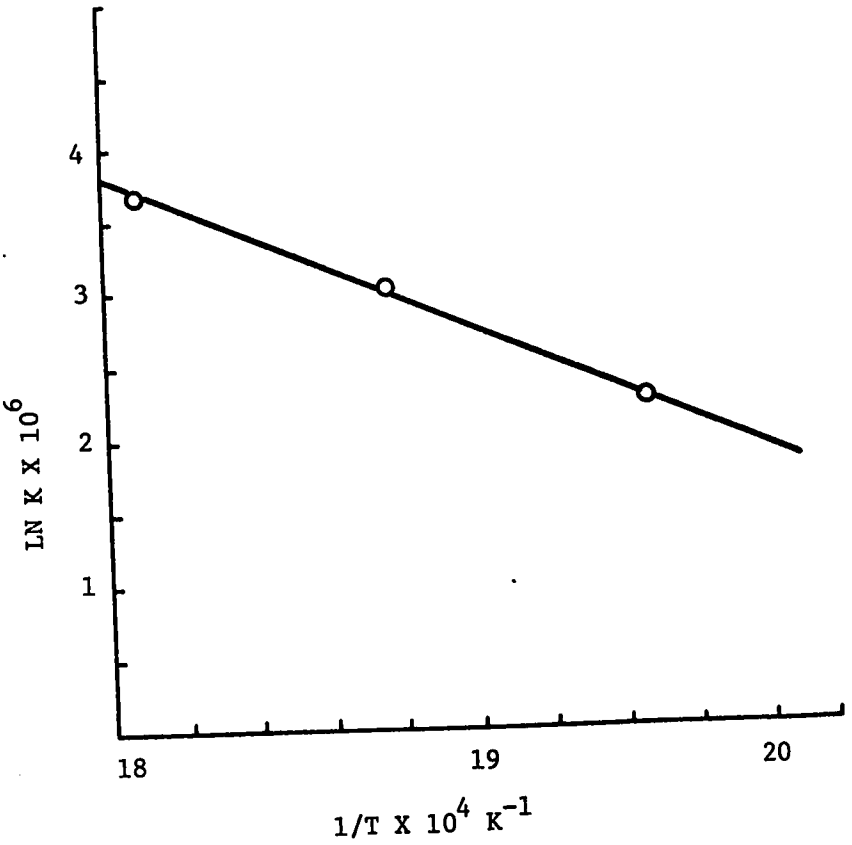


Figure 22:LN K Vs 1/T for carbon oxide

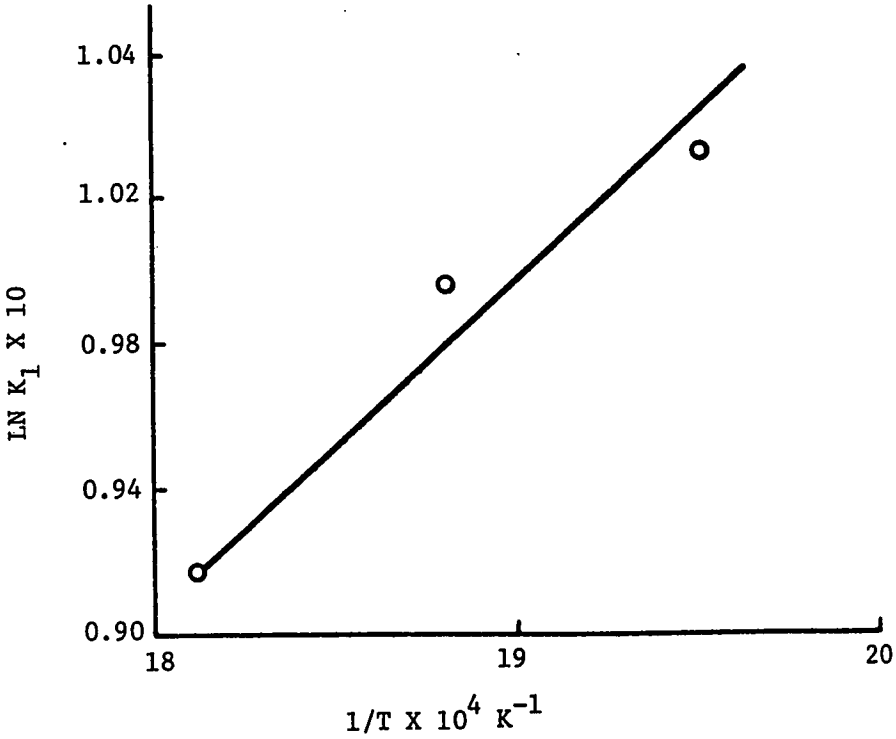


Figure 23: LN K_1 Vs 1/T for carbon oxide

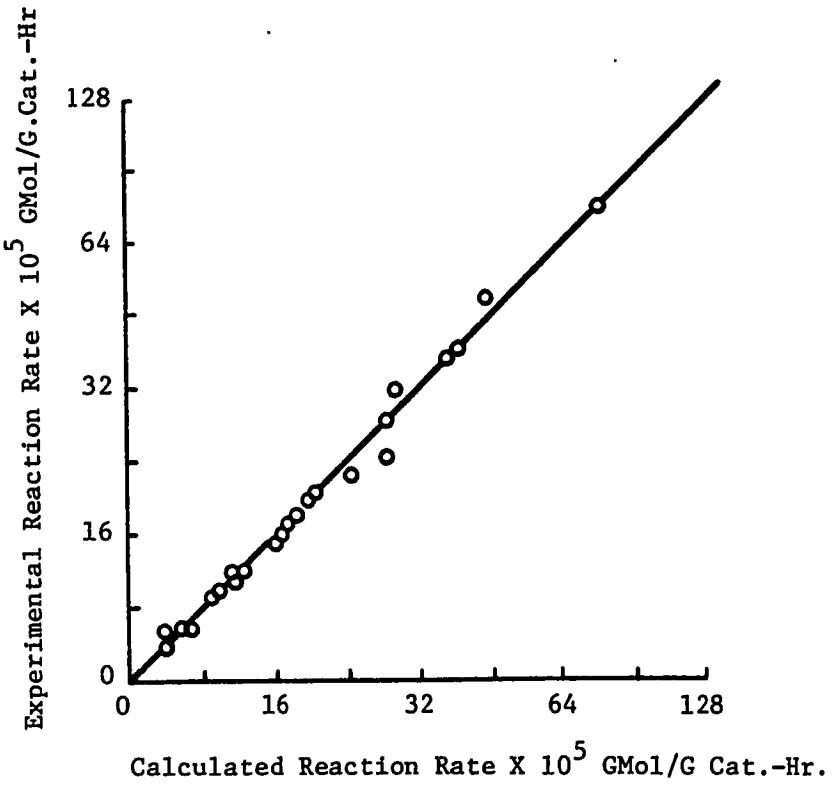


Figure 24: Experimental Reaction Rate
Vs Calculated

Table-12 Activation energies for the partial and complete Oxidation reaction of ethylene over Silver Catalysts

Author(year)	Activation energy(kJ/mole)	
	C2H4O	CO2+H2O
Twigg(1946)	67	67
Murray(1950)	50	63
Wan Shen-Wu(1950)	81	
Kurilenko(1958)	64	83
Alfani(1970)	36	31
Force(1975)	E1=E2	E1=E2
Kripylo(1979)	105	99
Dettwiler(1979)	77	63
Present work	95	102

chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 *Conclusions*

a) The emperical rate equations for the ethylene oxidation on commercial silver catalyst(8% silver) supplied by Harshaw/Filtrol partenership are:

1) Rate of conversion of ethylene to ethylene oxide(gmol/gcat.-hr):

$$r_1 = \frac{(1.354\times10^{3})\exp(-9010/T)(P_{O2})^{0.5}(P_{C2H4})^{0.6}}{1+(2.88\times10^{-2})\exp(2400/T)(P_{CO2})}$$

2) Rate of conversion of ethelene to carbon dioxide (gmol/gcat.-hr):

$$r_2 = \frac{(6.30\times10^{3})\exp(-10800/T)(P_{O2})^{0.5}(P_{C2H4})^{0.5}}{1+(1.57\times10\text{-}2)\exp(1530/T)(P_{CO2})}$$

b) the intrapellet resitances are minimal

c) The interphase mass and heat transfer resistances are minimal

d) These rate expressions (free of any physical resistances) can be coupled with mass and heat transfer correlations to design commercial reactor .

e) Selectivity of ethylene oxide was observed to decrease with increase in total conversion of ethylene .

f) Temperature has a minor effect on selectivity of ethylene oxide .

g) Carbon dioxide has an inhibition effect on both the formation of ethylene oxide and carbon dioxide .

6.2 *Recommendations*

a) Using catalysts with different surface composition is helpful to investigate the effect of varying the surface composition on the kinetics of the reactions .

b) Injecting the products with the feed gas will lead to a better understanding of the carbon dioxide inhibition and its extent .

c) Employing different total pressures is helpful to investigate if such a change has an effect on the kinetics .

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APPENDICES

APPENDIX A

Sample calculation :

Run no. 24 is chosen for sample calculation .Mole fractions obtained from the chromatograph are corrected using the responce factores . Since the reactor is a CSTCR , reacrion rates were calculated by simply

$r_{C2H4}=F_A X / W$

x is the conversion

F_A is the inlet moles of Ethylene

w is the weight of the catalyst

defining X1, X2 as the conversions of ethylene to ethylene oxide and carbon dioxide respectively ,then

$r_{C2H4-C2H40} = F_A X1 / W$ (1)

$r_{C2H4-C02} = F_A X2 / W$ (2)

conversions were defined as

X1 = (C2H40)/[(C2H40)+ 0.5(C02)+(C2H4)]

X2=(0.5(C02)/[(C2H40)+(0.5(C02)+(C2H4)]

Selectivoty is defined as (C2H40) / [(C2H4+0.5(C02)] *100

So for run no. 24 , outlet composition is shown in the sample chromatogram .Using the correcting responce factors , The following correcred composition is obtained

compound	composition %
N2	77.39
02	16.32
C02	1.247
C2H4	2.918
H20	1.247
C2H40	0.8793

Then , $F_{C2H4}=(Q) (C_{C2H4})_{in}$ = 0.1003 mol/hr

X1 = 0.8793/(0.8793+.5*1.247+2.918)=0.199

X2 = .5*1.247/(0.8793+.5*1.247+2.918)=0.141

Selectivity= 0.8793/(0.8793+.5*1.247)= 58.5%

W=63.25g

So, using equations (1) and (2) , the following reaction rates were obtained

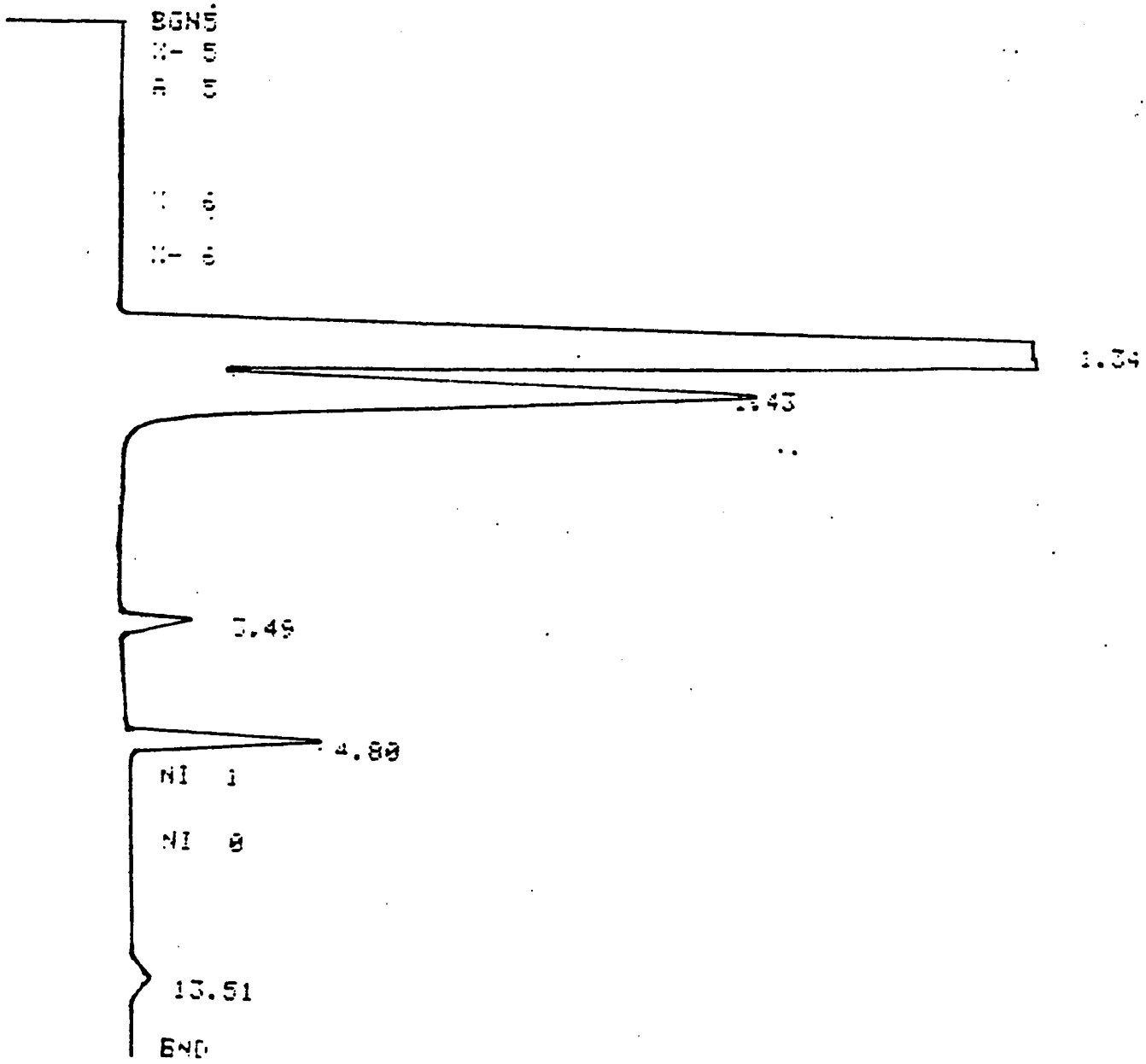
$r_{C2H4-C2H40}$= 3.16e-4 gmol/gcat-hr

$r_{C2H4-C02}$ = 2.24e-4 gmol/gcat-hr

ANAL 1 DET 1 METH 1 1 FILE 18

RUN 11

SENSITIVITIES 100 8



ANAL 1 DET 1 METH 1 1 FILE 18

RUN 7 9 : 35.9 0 / 0 / 0

SENSITIVITIES 100 8

TIME	AREA	BC	RRT	RF	C	NAME
0.36	0.0269		0.036	1.000	0.0923	
1.34	22.8377	T	0.134	1.000	78.1586	NITROGEN
1.43	4.4766		0.143	1.000	15.3206	OXYGEN
2.45	0.0048		0.245	1.000	0.0164	
3.49	0.4428	V	0.349	1.000	1.5156	CARBON DIOXIDE
4.80	1.0622	T	0.480	1.000	3.6352	ETHYLENE
13.51	0.3685		1.351	1.000	1.2613	ETHYLENE OXIDE

Figure 25. Sample chromatograph

APPENDIX B

Reactor performence :

The degree of mixing in the reactor was determined by Berty [34] , by a step change in the concentration of helium tracer in nitrogen . A plug flow reactor in series with an ideal mixer model was used for the analysis of mixing problem . Since the only observable daviation from the ideal behavior was assumed to be a time delay , the model used is as follows :

$$C/C_S = \exp(-\eta (t-\lambda)/\tau)$$

where C/C_S is the ratio of decaying helium concentration to the steady state concentration that existed before hilium shut off. τ is the residence time , η is the effectiveness factor for mixing , λ is the lag time .

The close approximation to the ideal mixing and uniformity in the flow was experimentally verified by Berty [34] , at a minimum recycle ratios of 20 .

Calculation of the blower :

Leva equation for pressure drop through a fixed bed is

$$\Delta p/q = \Delta h = [4 f_m(1-\epsilon)^{3-n}/(\phi^{3-n}\epsilon^3)](L/D_p)(V^2/2g)$$

The n of Leva's equtsion is 1.96 approching 2.00 , and f_m is ciose to 1.0. For these conditions the Leva equation simplified to

$$\Delta h = [4(1-\epsilon)/\phi\epsilon^3)(V^2/2g)$$
$$= K(v^2/2g)$$

For the original calibrated catalyst , K for a depth of one particle diameter was found to be 16 , Berty(34).

For the catalyst in this work

D_p= 3.9mm

L= 24mm

ϵ = 0.40

n~ 2.0

f_m~ 1.0

$1-\phi/\epsilon^3 = 9.38$

$1/\phi = 1.1$

$1-\epsilon/\phi\,\epsilon^3 = 8.52$

then applying Leva's equation

$K = 17.17$ for $L/D_p = 1$

L/D_p in this investigation is 6.10

Then $\Delta h = 104$

The for the blower is

$\Delta h = 1.1(RPM/1000)^2$, Berty(34)

this is a characteristic for the blower

Since the two pressures must be equal , those combine to give

$RPM = 2200\ V$

or

$V = 0.46(RPM/1000)$

Calculation of the recycle ratio :

v=.46 m/s at rmp=950

Q=12.0 cu. cm at reaction conditions(300 psia,280 C)

where Q is the inlet flow rate

Q inside = (A)(V)

=(14.4)(46)

= 638 cu. cm /s

R(recycle ratio) = 638/12.0

= 53

recommended minimum is 20

APPENDIX C

Estimation of transport effects :

Reaction rates chosen are those the highest at T=280 C.

$Re = D_p G / \mu$

G= mass velocity (Vq)=5.72 Kg/m^2S

D_p=0.0039m

μ_{air}=0.025cp

$\mu_{ethyl.}$=0.013cp

Re=930

Then to estimate the external mass transfer , the following correllation is used

$C_b - C_s = r_p (\mu/qD)^{2/3} / a_t (G/q) J_d$

r_p= reaction rate per unit of catalyst = 8.15e-4 gmole/gcat-hr

a_t=external surface area per unit mass of catalyst

= $0.001 m^2/g$

J_d=J-factor = $(.458/.40)(Re)^{-.407}$=0.0709

D was determined by using the Chapman Enskog

$D_{air-ethyl.}$=0.0085 m^2/hr

then Schmidt no. (μ/qD)=0.782

so $C_b - C_s$=6.2e-6 gmole/l

or $P_b - P_s = 4.1e-3$ psia

thus indicating the absence of external mass transport

For external heat transfer estimation , the following correllation is used

$$T_s - T_b = r_p(-\Delta h)(C_p\,\mu/K_f)\,/(a_t)(J_h)(C_p)(G)$$

$C_p\,\mu/\,K_f$ = Pr no. = 0.69 for air at 280 C

ΔH= heat of the reaction = -1217 E3 j/gmole

J_h=J-factor =J-factor calculated previously =0.0709

C_p= heat capacity= 0.24 cal/g C

so $T_s - T_b$= 0.42 K

Thus indicating negligibal external heat transfer limitation .

For estimation of the intraparticle mass and heat transfer limitations , the following criteria is used

$$\phi = r_p\, q\, L^2 / [(D_e\, C_g)](e^{\beta\partial(1+\beta)})$$

L=pellet radius = 0.00159m

D_e=effective divusivity

C_g= bulk gas concentrarion(ethylene)=0.01e3 gmole/m^3

q=pellet density=2.1 g/cm^3

ß,∂ are defined by the following eqtions

$\partial = E/R\ T_s$

$ß = (-\Delta h)(D_e)(C_s)/\ K_e\ T_s$

E= activation energy(E/R)=10800

R ideal gas law constant

Ts= Temperature at the surface of the catalyst=553K

Ke= effective conductivety =0.2 BTU/hr-ft-f

now,

De=D ¢/Ω

D= 0.0085 using Chapman -Enskog formula

¢=catalyst particle void fraction=0.50 approximately

Ω=trtuosity=4 approximately

so

De= 0.00295m2/hr

∂=19.5

ß=0.015

then substituting

ø=0.19 <1

thus indicating that intraparticle resestance is negligable

APPENDIX D : summary of experimental data

RUN NO. = 1

TEMPERATURE(C) = 260

FLOW RATE (l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7831
02	0.1927	0.1543
C2H4	0.0512	0.0352
C02	0.0000	0.0111
H20	0.0000	0.0111
C2H40	0.0000	0.0052

RUN NO. = 2

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7815
02	.1927	0.1551
C2H4	0.0512	0.0376
C02	0.0000	0.0100
H20	0.0000	0.0100
C2H40	0.0000	0.0057

RUN NO.	= 3
TEMPERATURE(C)	= 260
FLOW RATE(l/HR)	= 25.4
RPM	= 950
PRESSURE (PSIG)	= 300
CATATYST (8% Ag)	= 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7802
02	0.1927	0.1543
C2H4	0.0512	0.0392
C02	0.0000	0.0099
H20	0.0000	0.0099
C2H40	0.0000	0.0067

RUN NO. = 4

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7755
02	0.1927	0.1584
C2H4	0.0512	0.0388
C02	0.0000	0.0102
H20	0.0000	0.0102
C2H40	0.0000	0.0069

RUN NO. = 5

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7739
O2	0.1927	0.1597
C2H4	0.0512	0.0381
CO2	0.0000	0.0105
H2O	0.0000	0.0105
C2H4O	0.0000	0.0072

RUN NO. = 6

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7743
02	0.1927	0.1584
C2H4	0.0512	0.0376
C02	0.0000	0.0108
H20	0.0000	0.0108
C2H40	0.0000	0.0081

RUN NO. = 7

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7764
O2	0.1927	0.1564
C2H4	0.0512	0.0370
CO2	0.0000	0.0112
H2O	0.0000	0.0112
C2H4O	0.0000	0.0078

RUN NO. = 8

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7753
02	0.1927	0.1568
C2H4	0.0512	0.0369
C02	0.0000	0.0115
H20	0.0000	0.0115
C2H40	0.0000	0.0081

RUN NO. = 9

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7741
02	0.1927	0.1575
C2H4	0.0512	0.0366
C02	0.0000	0.0118
H20	0.0000	0.0118
C2H40	0.0000	0.0082

RUN NO. = 10

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7786
02	0.1927	0.1570
C2H4	0.0512	0.0367
C02	0.0000	0.0119
H20	0.0000	0.0119
C2H40	0.0000	0.0081

RUN NO. = 11

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 9.25

RPM = 350

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7703
O2	0.1870	0.1464
C2H4	0.0660	0.0395
CO2	0.0000	0.0173
H2O	0.0000	0.0173
C2H4O	0.0000	0.0088

RUN NO. = 12

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 9.25

RPM = 650

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7708
02	0.1870	0.1421
C2H4	0.0660	0.0378
C02	0.0000	0.0198
H20	0.0000	0.0198
C2H40	0.0000	0.0096

RUN NO. = 13

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 9.25

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7716
02	0.1870	0.1398
C2H4	0.0660	0.0370
C02	0.0000	.02118
H20	0.0000	.02118
C2H40	0.0000	0.0092

RUN NO. = 14

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 51.0

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7608	0.7719
02	0.1952	0.1718
C2H4	0.0400	0.0336
C02	0.0000	0.0077
H20	0.0000	0.0077
C2H40	0.0000	0.0074

RUN NO. = 15

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 106

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7737	0.7774
02	0.1889	0.1782
C2H4	0.0374	0.0297
C02	0.0000	0.0042
H20	0.0000	0.0042
C2H40	0.0000	0.0062

RUN NO. = 16

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 275

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7815	0.7843
02	0.1853	.1797
C2H4	0.0333	.0273
C02	0.0000	0.0023
H20	0.0000	0.0023
C2H40	0.0000	0.0041

RUN NO.	= 17
TEMPERATURE(C)	= 240
FLOW RATE(l/HR)	= 9.25
RPM	= 650
PRESSURE (PSIG)	= 300
CATATYST (8% Ag)	= 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7515
02	0.1870	0.1677
C2H4	0.0660	0.0431
C02	0.0000	0.0143
H20	0.0000	0.0143
C2H40	0.0000	0.0091

RUN NO. = 18

TEMPERATURE(C) = 240

FLOW RATE(l/HR) = 9.25

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7521
02	0.1870	0.1633
C2H4	0.0660	0.0438
C02	0.0000	0.0155
H20	0.0000	0.0155
C2H40	0.0000	0.0099

RUN NO. = 19

TEMPERATURE(C) = 240

FLOW RATE(l/HR) = 9.25

RPM = 650

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7510
O2	0.1870	0.1651
C2H4	0.0660	0.0441
CO2	0.0000	0.0151
H2O	0.0000	0.0151
C2H4O	0.0000	0.0093

RUN NO. = 20

TEMPERATURE(C) = 240

FLOW RATE(l/HR) = 9.25

RPM = 350

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7523
02	0.1870	0.1619
C2H4	0.0660	0.0448
C02	0.0000	0.0158
H20	0.0000	0.0158
C2H40	0.0000	0.0095

RUN NO. = 21

TEMPERATURE(C) = 280

FLOW RATE(l/HR) =9.25

RPM = 650

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7481
02	0.1870	0.1428
C2H4	0.660	0.338
C02	0.0000	0.0339
H20	0.0000	0.0339
C2H40	0.0000	0.0075

RUN NO.	= 22
TEMPERATURE(C)	= 280
FLOW RATE(I/HR)	=9.25
RPM	= 350
PRESSURE (PSIG)	= 300
CATATYST (8% Ag)	= 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7529
02	0.1870	0.1431
C2H4	0.0660	0.0344
C02	0.0000	0.0311
H20	0.0000	0.0311
C2H40	0.0000	0.0074

RUN NO. = 23

TEMPERATURE(C) = 280

FLOW RATE(l/HR) = 9.25

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7483
O2	0.1870	0.1414
C2H4	0.0660	0.0335
CO2	0.0000	0.0347
H2O	0.0000	0.0347
C2H4O	0.0000	0.0075

RUN NO.	= 24
TEMPERATURE(C)	= 280
FLOW RATE(l/HR)	= 51.0
RPM	= 950
PRESSURE (PSIG)	= 300
CATATYST (8% Ag)	= 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7608	0.7739
02	0.1952	0.1632
C2H4	0.0139	0 .0292
C02	0.0000	0.0125
H20	0.0000	0.0125
C2H40	0.0000	0.0088

RUN NO. = 25

TEMPERATURE(C) = 280

FLOW RATE(l/HR) = 106

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7737	0.7761
02	0.1889	0.1748
C2H4	0.0374	0.0279
C02	0.0000	0.0072
H20	0.0000	0.0072
C2H40	0.0000	0.0068

RUN NO. = 26

TEMPERATURE(C) = 280

FLOW RATE(l/HR) = 275

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7815	0.7850
02	0.1853	0.1769
C2H4	0.0333	0.0259
C02	0.0000	0.0039
H20	0.0000	0.0039
C2H40	0.0000	0.0048

RUN NO. = 27

TEMPERATURE(C) = 280

FLOW RATE(l/HR) = 9.25

RPM = 350

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7471	0.7558
02	0.1870	0.1429
C2H4	0.0660	0.0328
C02	0.0000	0.0306
H20	0.0000	0.0306
C2H40	0.0000	0.0073

RUN NO. = 28

TEMPERATURE(C) = 240

FLOW RATE(l/HR) =51.0

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7608	0.7706
02	0.1952	0.1789
C2H4	0.0440	0.0366
C02	0.0000	0.0042
H20	0.0000	0.0042
C2H40	0.0000	0.0055

RUN NO. = 29

TEMPERATURE(C) = 240

FLOW RATE(l/HR) = 106

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7737	0.7729
O2	0.1889	0.1852
C2H4	0.0374	0.0332
CO2	0.0000	0.0024
H2O	0.0000	0.0024
C2H4O	0.0000	0.0038

RUN NO. = 30

TEMPERATURE(C) = 240

FLOW RATE(l/HR) = 275

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7815	0.7801
02	0.1853	0.1850
C2H4	0.0333	0.0301
C02	0.0000	0.0011
H20	0.0000	0.0011
C2H40	0.0000	0.0019

RUN NO. = 31

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7972
02	0.1927	0.1484
C2H4	0.0512	0.0235
C02	0.0000	0.0093
H20	0.0000	0.0093
C2H40	0.0000	0.0123

RUN NO. = 32

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7734
O2	0.1927	0.1532
C2H4	0.0512	0.0414
CO2	0.0000	0.0147
H2O	0.0000	0.0147
C2H4O	0.0000	0.0093

RUN NO. = 33

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7719
O2	0.1927	0.1567
C2H4	0.0512	0.0398
CO2	0.0000	0.0122
H2O	0.0000	0.0122
C2H4O	0.0000	0.0090

RUN NO. = 34

TEMPERATURE(C) = 260

FLOW RATE(l/HR) = 25.4

RPM = 950

PRESSURE (PSIG) = 300

CATATYST (8% Ag) = 63 gram

	MOLE FRACTION IN	MOLE FRACTION OUT
N2	0.7561	0.7727
02	0.1927	0.1581
C2H4	0.0512	0.0384
C02	0.0000	0.0114
H20	0.0000	0.0114
C2H40	0.0000	0.0088